VOLUME TWO – 1966

CASE HISTORIES OF ACCIDENTS IN THE CHEMICAL INDUSTRY

MCA MANUFACTURING CHEMISTS ASSOCIATION

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CASE HISTORIES OF ACCIDENTS IN THE CHEMICAL INDUSTRY

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FOREWORD

Since 1951, member companies of the Manufacturing Chemists Association have voluntarily cooperated in the Association's safety program by submitting case histories of accidents or near-accidents occurring in chemical plants. Behind this unique joint endeavor is the compelling concern of industry management for the welfare of industry employees. It reflects an open resolve by leaders of the industry that any mistakes or omissions of today will not be repeated tomorrow.

Accident case histories are written by plant foremen, operating personnel, or other local company representatives. They are edited only when necessary to preserve a standard format and are reproduced monthly by MCA's Safety and Fire Protection Committee. Since they are submitted on a confidential basis the company name is not divulged.

Industry reception of this monthly publication has been encouraging. Many companies engaged in operations similar to those described in particular case histories have adopted recommended preventive measures. A number of companies purchase multiple copies of the monthly issue for distribution to plants, where they are read and studied.

This is the second in a series of volumes compiling these accident case histories. It contains case histories published 1960 through 1965. Volume One, available for $2.50 per copy, contains case histories published 1951 through 1959.

MCA's Safety and Fire Protection Committee is grateful to companies which have cooperated in the accident case history program. It looks for increasing cooperation. Those who find this volume helpful are asked to contribute to future issues by submitting to MCA, case histories of accidents or near-accidents should they occur.

The case histories contained in this volume have been submitted in good faith by the chemical companies which experienced the accident or incident described. No warranty, guarantee, or representation is made by the Manufacturing Chemists Association as to the correctness or sufficiency of any information, statement of accident cause, or recommendations for preventive measures contained herein or that other or additional measures may not be required.

CASE HISTORIES
of
Accidents in the Chemical Industry

CASE HISTORY NO. 597

Accident Discharging Caustic Potash

Description: An operator was unloading a tank car ot 45 per cent technical grade KOH. After adding 26 inches of KCl brine to the blend tank, he proceeded to the south loading dock and inspected the tank car for cleanliness, inserted the loading hose and opened the loading line discharge valve.

He then proceeded to the KOH loading pump at the north end of the Chlorine Department and after putting on his goggles, opened the loading pump 3 inch discharge valve. He then opened the dilution water diaphragm valve (2 or 3 turns), which connects the water supply to the suction side of the loading pump. The rubber hose water connection immediately ruptured, spraying his face and head with 50 per cent KOH draining back through the pump from the open discharge line.

After closing the diaphragm valve, he walked to a safety shower (60 ft. away) with goggles still in place. At the emergency shower he began flushing the caustic off with the eye bath hose, keeping his head tilted to protect his right ear. While washing, his hat fell off and also the goggles, since they were attached, and KOH was washed into his right eye.

Cause: It is the Committee's opinion that the accident resulted from rupture of the dilution water inlet rubber hose line caused by deterioration of the hose and back pressure on the hose from the open loading pump discharge line. Significant details are:

1. Two rubber hoses with connectors are used to connect city water, or softened water to the dilution water valve. Both hoses indicated deterioration. The softened water hose was of questionable age but was not involved. The city water hose connection in use at the time was approximately 8 weeks old.
2. The present method of diluting 50 per cent KOH with water and KCl brine is to open the pump discharge valve before starting the pump.
3. The common practice of permanently securing goggle straps to safety hats must be avoided. It was after the injured lost his hat and goggles that KOH washed into his eye.
4. Other personnel in the area were not aware of the operator's trouble until he left the shower and walked to the Chlorine Department control room.

It is the Committee's opinion that the accident could have been avoided if permanent dilution water piping was installed, and a reverse flow check valve and pressure bleed valve installed at the dilution water inlet connection.

Preventive Measures:

1. The Committee's immediate recommendation to install new rubber hoses was completed the day of the investigation.
2. Install permanent piping from the softened water and city water headers to the dilution inlet valve connection, complying with state regulations and safe design practice. Include reverse flow check valve and pressure bleed valve at water dilution inlet connection.
3. Mandatory safety regulation that under no circumstance should goggles be permanently attached to safety hats. When using goggles, straps should be worn around the head and not the safety hat.
4. Investigate use of protective plastic sleeves and covers for caustic valves and connections.

5. Investigate all usage of rubber hose in corrosive service.

6. Set up routine quarterly inspection and pressure testing procedure for rubber hose applications.

7. Install alarm system activated by operation of safety showers to alert other personnel in the immediate area that assistance is needed.

8. Investigate all city water connections to process piping and make necessary design changes and/or additions to assure no feed back of process material into the city water system.

CASE HISTORY NO. 598

Rupture of Aqua Ammonia Tank

Description: In the manufacture of ammonia synthesis gas the purification includes the scrubbing of the gas at approximately 2000 psig with a weak solution of aqua ammonia. This solution is injected into the scrubber by a high pressure pump. The solution passes down through the tower and is removed from the base of the unit by a level controller, returning to a 2000 gallon vertical hold-up tank.

The 3/4-inch level control valve equipped with 1/4-inch trim failed in an open position allowing the liquid and gas in the scrubber to be released into the hold-up tank which is equipped with a 2-inch atmospheric vent. The surge of gas into the hold-up tank caused a rupture of the vessel. The tank head was blown upward shearing the vent line then striking and damaging an overhead conduit rack before coming to rest on the ground near the base of the tank. The supporting steel for the tank head was blown upward about 50 feet. The escaping gas, containing approximately 75 per cent hydrogen, immediately ignited causing a fire. Soon after the failure occurred the valves in the control valve piping were closed, stopping the flow of gas. Water was used to quench the tank.

Production rate was cut to a minimum while surveying the damage and preparing a tank of solution. Production was returned to normal by controlling the level by hand until a control valve could be installed downstream of the one which failed.

Cause: The exact cause of the level control valve to fail in the open position has not been determined. However, it has been assumed that the control valve trim failed.

Preventive Measures: A survey is being made of similar equipment in the plant which could cause an accident. The safety factor of vent systems will be increased.

CASE HISTORY NO. 599

Laboratory Accident Using Perchlorate Mixture

Description: A chemist was carrying out a procedure which involved about 2 grams of an exceptionally powerful perchlorate mixture.

The material was being heated in a small test tube held manually with a test tube holder inserted in a silicone oil bath which was in a 250 ml. glass beaker on an electric hot plate, enclosed in a portable hood made of 18 ga. stainless steel with 1/4-inch safety glass doors. The doors were in the fully opened position which allowed an open area 18 x 30 inches at the right side of the hood.

The temperature of the bath was approximately 150°C as indicated by a thermometer in the bath which was not stirred. The chemist seated in front of the hood noticed a frothing in the test tube, which he was stirring with a metal spatula. Just at this time, a lab technician had reached into the hood to place a 50-ml. test tube containing another material into the bath from the left side of the chemist. In so doing, he partially obscured the vision of the chemist. Almost immediately, an explosion with a flash of flame occurred followed by a cloud of carbonaceous smoke.

The beaker and test tube were reduced to fine particles approximately 10 mesh or smaller. The hot plate struck one of the safety glass doors, cracking it. The force of the explosion dented the aluminum top of the hot plate and rendered it useless. The laboratory bench, approximately 1-1/2 inches thick, was cracked. The hood contained the force of the explosion except for the opening in front.

The chemist received multiple abrasions of all fingers, hands, face and lips.

A laboratory technician standing at the hood received similar burns and abrasions of all fingers of the right hand, right wrist and back of right hand, upper abdomen and burns of the face.

Cause: It is difficult to determine the cause of this explosion. The inherent hazards involved in this type of research are well known and explosions, detonations, or very rapid combustion are to be expected.

It is possible that this material foamed over and dropped into the silicone bath, which ignited. Silicone oil, upon repeated heating to high temperature, may break down and form materials of lower flash point than the original oil, which was Silicone 550. It is quite probable that the carbonaceous smoke was due to this type of breakdown.

It is possible this oxidizer mixture may have been sufficiently sensitive to heat and friction from stirring to cause it to detonate.

It would appear that if the protective glass doors had been used in the proper manner as designed that the chemist would have received much less of the force of the explosion on his face and chest.

It is also evident that protection for hands and forearms is needed.

Preventive Measures: Standard procedures for experimental work are to be written by the Group Leader and Safety Director. These are to be enforced. The rules will include:

1. Quantities not greater than 1/2 gm. perchlorate.
2. Leather gloves must be worn.
3. Leather gauntlets or sleeves must be worn.
4. Safety glasses with side shields or goggles must be worn.
5. Face shield to be used when hood must be opened.
6. Hoods to be used by one person only during a reaction.
7. Suitable warning to be placed near hood during reaction for protection of other personnel.
8. Hood doors to be adjusted to provide protection to face and chest.
9. Test tube and thermometer must be supported other than manually.
10. A minimum amount of equipment may be set up in a hood.
11. Silicone oil baths should be changed when substantial discoloration is observed. Discoloration is an evidence of depolymerization and formation of components more volatile than the original oil.

CASE HISTORY NO. 600

Accident Filling Drums From Tank Car

Description: An employee was filling 55 gallon drums with a chlorinated hydrocarbon drawn from a tank car. A high-speed pump was being used. When the tank car became empty, air surged into the drum being filled. The material sprayed from the bung of the drum striking the employee in the face.

Cause: The pump was being used to fill the drums because the tank car was not spotted properly. This was due to crowded track conditions. Normally this material is transferred to drums by gravity.

Preventive Measures: When improper spotting requires use of pumps, the area around the drum bung will be shielded so as to prevent spraying of chemical. Employees will wear protective clothing and face shield in addition to safety glasses when drumming off corrosive materials.

CASE HISTORY NO. 601

Phosphoric Acid Released

Description: A small leak was noted from the weld of a reducing nipple between the discharge nozzle of the phosphoric acid storage tank and the shut-off valve. Considering that the acid tank had a considerable quantity of acid in it, it was decided to patch the leak temporarily until the acid was used and the tank empty. This was done by means of a clamp and red rubber packing directly on the pipe. Because of the acid corrosiveness, it was impossible to empty it into steel drums or other steel tanks. Rubber lined vessels were not available.

The next day, the leak had started again and the clamp was removed and relocated in order to stop the leak. While this was done, it was noticed that the corrosion in the pipe had extended and that the pipe wall was very thin.

By the second day, the leak became much greater and at 4:00 p.m. it was decided to remove the nipple and place a valve immediately at the discharge nozzle flange. The level in the tank was 1.90 meters.

The work had been programmed to be done by the contractor's mechanic who put on acid-proof boots, trousers, jackets and hoods. The shift supervisor was at the site protecting the men with a water hose. The operators were also present in order to assist the mechanics.

Once the bolts of the flange to be removed were loosened, a blind flange was slipped between the other two flanges and the bolts removed. The pipe section was removed and the pressure in the tank was more than could be held by the person holding the blind flange against the nozzle so the flange was forced away and the full acid jet flowed freely. In view of this condition, the mechanic got a toilet flusher and jammed the rubber end into the nozzle. During this operation the acid spilled was copious and the force of the jet very difficult to overcome. The operators had to help hold the plug in place.

Once the plug had stopped the flow of acid, the valve was immediately bolted on to the flange and closed.

Cause: The corrosion of the stainless steel pipe beginning at the weld and continuing into the pipe proper was the main cause, plus the fact that it was not possible to empty the tank before the spillage took place. Also, the type of hood used was not the best because the intoxication could have been avoided if the hoods had had an air line attachment to keep the man supplied with fresh air.

Preventive Measures:

1. Obtain two complete rubber suits including hoods of the kind that can be connected to an air line in order to have four units available in the plant.

2. Wherever a hazardous operation is to be performed, it should be planned ahead of time as thoroughly as possible and maintenance, production and safety should be discussed.

3. A supervisor should be at the site during the operation, preferably the production supervisor and the maintenance supervisor of the area. If not possible, one of the shift supervisors should be notified so that he is present.

4. Establish as a plant safety rule that on all tanks the outlet valve be located as close to the tank as possible.

CASE HISTORY NO. 602

Operator Sprayed with Aniline

Description: The caution flag was waving on the morning of November 18, 1959. Two operators were charging aniline to #11 reactor. They were using fresh aniline although the recovered aniline measuring tank showed 42 inches on the gauge glass. The material would not flow from the measuring tank and an effort had been made to make the material flow by steaming the bottom line. Previous shifts had had the same trouble.

One of the operators tried again and got the material to move down about 2 inches on the gauge glass. He turned the steam on again for a second try, walked past the tank, descended the ladder and as his head was at platform level, the tank ruptured. He was sprayed with aniline on the face, neck, eyes, hands, and clothing; the thick clothing kept most of it from his skin. He went to the locker room where he could get soap and hot water to remove the aniline.

Cause: The tank vent line was plugged. Plugging was caused by inadequate vent size.

Preventive Measures:

1. Install a new tank with adequate vents.

2. As an alternate to Recommendation No. 1, eliminate the need for the tank.

3. Immediately blank off all piping, remove debris and anchor wreckage.

4. Establish a committee to supplement current work on venting, with particular emphasis not only on vent sizes, but on services that may plug. The committee should establish a check list for use by department supervision to safety audit all department tanks. Adequate sight glasses, vent lines, pop valves and rupture discs should be a part of this check list.

5. Since this is the second near-miss in this department in the last few months, an all-out effort should be made to push the project to upgrade the general area.

CASE HISTORY NO. 603

Laboratory Fatality Opening Bottle of Isopropyl Ether

Description: The victim was fatally injured while trying to open a bottle of isopropyl ether. Each chemist keeps a supply of reagents and solvents in an assigned section of a central storage area and only takes small quantities to his laboratory as he needs them. Dr. X, who had been with company about three years, had apparently inherited some of the supplies which were in his section of the storage room from his predecessor. Needing some isopropyl ether, he found a pint glass bottle so labeled on the shelf and took it to the next room where he attempted to open it over a sink. The cap appeared to be stuck tightly and he grasped the bottle in one hand, pressed it to his stomach and twisted the cap with the other hand. Just as the cap broke loose the bottle exploded, practically disemboweling the man and tearing off several fingers. While no one else was in the room at the time, another employee was just outside in the corridor and reached the victim just as he fell, and it was but a few minutes before they had first aid assistance and, shortly thereafter, a doctor. The victim remained conscious and, in fact, quite coherent for some time, and was able to describe exactly how the accident happened although he did not try to explain the cause.

The man was taken to a hospital within a few minutes and immediately put under anesthetic while several doctors worked over him to try to save his life. However, he was bleeding so badly from internal injuries that the doctors could not keep him alive. He died within two hours of the accident of "massive internal hemorrhage."

Cause: It was concluded that this accident was caused by peroxides which formed in the ether while it sat on the storage shelf. Isopropyl ether is considered one of the worst offenders in this respect. As the ether ages it forms peroxides, which, however, are not stable and which further react to form additional potentially dangerous by-products in solution, such as triacetone peroxide. These materials are very unstable and it is thought that some of the peroxides may have crystallized in the threads of the cap and exploded when the cap was turned. Light, air (or oxygen) and heat accelerate the formation of peroxides in isopropyl ether; it is therefore stored or shipped in containers of metal or dark brown glass. Iron apparently inhibits the formation of peroxides, and glass bottles of ether sometimes have iron wires suspended from the stoppers. Ethers stored in iron containers reportedly do not form peroxides, or at least form them very slowly.

It was stated that after the accident the stockroom was searched and two metal cans of the isopropyl ether were found, the age of which was not known. The cans were taken to the back lot and fired upon with a shotgun. They were punctured but no explosion occurred.

Preventive Measures: The Safety Department has set up the following general rules for the Research Center to minimize the potential hazards of storing and using ethers. These rules must be observed.

1. Isopropyl ether and anhydrous ether must be purchased in small quantities and in iron containers if possible. The containers will be dated when placed in the storeroom, and be shielded from light and heat.

2. All ethers used in the laboratories must be kept in cans rather than in bottles.

3. Isopropyl, iso-amyl and anhydrous ethers will not be kept over six months, ethyl and other ethers not over one year.

4. Each time an employee fills his reagent container from the stockroom, he will be required to date the container. This practice should be followed with other solvents and reagents which are affected by light, air, or aging. Overage material (as in No. 3 above) must be destroyed. Frequent safety checks will be made, and overage supplies on laboratory shelves will be sufficient cause for reprimand.

5. All work involving ethers must be done behind safety shields. Safety shields also should be placed in front of reaction vessels or distillation apparatus involving ethers carried out in hoods. Safety glasses must be worn when handling ethers. Other protective equipment will be provided as required or requested.

6. When additives will prevent formation of peroxides and are not detrimental to the end product or end use of the ether, they should be used. For example, according to a manufacturer, "Isopropyl ether can form explosive peroxides on storage and should be distilled only after these peroxides have been tested and if present, destroyed. Peroxides can be decomposed by adding a small amount of a suitable reducing agent as 1-naphthol of sulfites. Peroxides also can be destroyed by adding one volume of aqueous 25% sodium hydroxide to two hundred volumes of the ether. A small amount of water added to isopropyl ether is a convenient method for reducing the tendency to form peroxides - if the water is not detrimental to the end use of the ether. Water at a concentration of 1%, based on the weight of the ether, is effective as an inhibitor.

Editor's Note: We received a request from the U.S. Public Health Service for advice on the safe disposal of 1000 cans of ethyl ether kept in storage in hospitals for 10-15 years. The ether, it was thought, contained some 3 percent peroxides. Was it safe to spike open the cans and burn the contents? At about the same time we received a similar request from a west coast hospital. What would be the safest procedure for disposal of about 30 gallons of isopropyl ether which had been stored in glass and metal containers for several years?

MCA case history, number 603, described a laboratory fatality when a bottle of isopropyl ether was opened. Here is an excerpt: "Needing some isopropyl ether, he found a pint glass bottle so labeled and took it to the next room where he attempted to open it over a sink. The cap appeared to be tightly stuck and so he grasped the bottle in one hand, pressed it to his stomach and twisted the cap with the other hand. Just as the cap broke loose the bottle exploded, practically disemboweling the man. . . ."

The following information has now been received in response to our inquiry as to whether a 3 percent peroxide content could present an explosion hazard:

"I have always been concerned with the tendency of ethers to auto-oxidize on long standing in air, and through its reported recovery and use in solvent extraction operations. I have had 'hand-me-down' advice chiseled into my brain by my 'elders' that one takes a risk with old ether, since there is always the chance of spontaneous formation of non-volatile peroxides (with unstable cyclic and oxonium structures) on standing in air, especially in sunlight, and that when ether is evaporated, or when a distillation is carried out to dryness, the overheated peroxide residue may explode violently. According to literature records, the composition and structure is subject to uncertainty. However, the following two compounds are known to have been identified in ethyl ether:

(1) $\underset{\text{OH}}{CH_3CH}O\cdot O\underset{\text{OH}}{CHCH_3}$ Dihydroxy diethyl peroxide

(2) $CH_3CH\langle\begin{smallmatrix}O\\O\end{smallmatrix}$ Ethylidene peroxide polymer

"Explosive peroxides can also form in isopropyl ether, which are more of an unknown composition (although ethylidine peroxide polymer is suspected – which, in the presence of water, decomposes to form acetone, hydrogen peroxide and isipropyl alcohol. The resultant acetone may react with hydrogen peroxide to form the unstable triacetone peroxide). In the case of ethyl ether, however, weak acid or water brings about a slow peroxide decomposition to hydrogen peroxide and ethyl alcohol.

"It is a rather broadly accepted practice in the better managed laboratories that all ethyl ether used for anesthetic purposes, or in processes that involve heating or distillation, must be essentially peroxide free and pass the U.S. Pharmacopeia XIII Standard Test with potassium iodide (which will detect about 0.001% peroxide reported as hydrogen peroxide--a brown-yellow color of liberated iodine will become apparent).

"One of the rules was to add, before distillation, a small amount of aqueous solutions of either ferrous sulfate or sodium sulfite and shake to destroy any peroxide present, whenever the above test was positive. Peroxides can also be decomposed by treatment with zinc dust, a small amount of sulfuric acid or acetic acid. In isopropyl ether, 1-napthanol may be added as an antioxidant, in concentrations of about 1 part in 10,000.

"Another common inhibitor trick is to use iron wire or certain other reducing metals and alloys. I also recall that special containers have been developed to prevent deterioration before use through the built-in presence of a lower oxide metal having more than one oxidation state, such as the sides and bottoms of tinplate containers being electroplated with a copper liner containing a small amount of cuprous oxide. I believe that stannous oxide is also used in the linings of tin containers.

"One of the serious pitfalls in laboratory handling of ethers as reagents is in the practice of transferring the ethyl ether from metal cans to glass bottles, particularly when glass-stoppered, when the protective effect of these metal cans is lost and the unsuspected influence of light (especially sunlight) is introduced. It is possible to gradually accumulate dried-out residues around the mouth and along the ground-joint between the glass stopper and the neck of the bottle. The forcing of a "frozen" stopper can produce enough friction to initiate an explosion.

"I have given some of this detail to indicate the need to provide preventive measures against having peroxides formed in the first place.

With regard to the disposal of the 1000 cans of the 10-15 year old ethyl ether which is stated to contain peroxides, I would not use the 3% figure as any safety measure, since on evaporation of the ether, this percentage just builds up in the apparatus, and when a dry point is reached, you just about have a 100% product. If one plans to salvage this quantity by adding ferrous sulfate and allowing time for reduction and removal of the peroxide (with actual test for its absence), some consideration should be given to the nature of the closure or stopper to safely permit this 'stabilization' treatment. Anything like this should be done under responsible and close supervision of a qualified chemist, who has the proper safety knowledge. This is only suggested where it may be desirable to recover this large amount and where extreme precautions would be taken as suggested.

"It would be much more preferable to destroy a few cans at a time by burning in a fire at some isolated dump site, with due regard for wind direction and sufficient barricading to prevent horizontal ejection of the cans in the event they become propėlled. Rather than spiking them for 'pressure venting', it would be better to perforate them at a safe distance by rifle fire. In any event, it would be well to have the fire department standing by in readiness at the burning site for any emergency."

CASE HISTORY NO. 604

Acid Splash When Filling Tank Truck

Description: The filling of a customer's tank truck with 93% sulfuric acid had just been completed and the operator was lifting out the loading pipe when the truck moved ahead unexpectedly. The driver jammed on the foot brake and the sudden stop caused acid to splash out of the open connection on top of the tank. The operator received splashes on his safety spectacles and about the face and left arm. The affected areas were immediately washed with water and first aid was obtained. Only minor burns resulted.

Cause: The engine was not running and no signal had been given to move the truck. Apparently the driver, who was sitting in the cab, had not set the hand brake and had put the truck in gear to hold it in position. Anticipating a move he evidently had his foot on the clutch and accidentally pressed the pedal.

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Preventive Measures: 1. Drivers of customers' trucks will be required to set the hand brake and retire to a specified nearby location until loading operations are completed.

2. Acid loading procedures will be reviewed with particular attention to personal protective equipment.

CASE HISTORY NO. 605

Acid Spill and Defective Safety Shower

Description: An employee was carrying a heavy walled 500 milliliter volumetric flask containing concentrated sulfuric acid to the sink. He held the flask by its stem, and when placing it on the sink he misjudged the distance and thereby knocked the flask against the edge of the sink, snapping off the stem and cascading acid down his left leg. The man immediately went under a safety shower and a co-worker pulled on the ring to release the water but the valve failed to open. When the ring was given another pull the valve handle sheared off at the valve stem. Fortunately, a quick-thinking fellow employee grabbed a bucket of ice water and poured it on the injured man's leg, drowning the acid.

Cause: 1. Investigation disclosed that the employee was not carrying the flask correctly.

2. Examination of the sheared valve handle indicated a slight wearing of the inside surface of the handle where it joins the valve stem assembly.

3. The angle of the valve handle was approximately straight up and down necessitating a great deal of force to activate the shower.

Preventive Measures: 1. All laboratory personnel will be reinstructed in the proper procedure for handling and carrying all volumetric flasks.

2. All safety shower handles will be readjusted so as to be in a 45° angle from the vertical.

3. The spring tension on the valve handles will be removed to allow the shower to remain in the open position when activated.

4. While safety showers in the Control Laboratories are checked every other day for general operability, a periodic visual check of all moving parts of the shower will be instituted to pick up any evidence of corrosion, erosion, binding and misalignment.

CASE HISTORY NO. 606

Fall from Hopper Truck

Description: The injured employee was preparing to load a hopper truck with finished product. He had positioned the loading spout directly underneath the finished storage bin into the hopper truck opening. While he was standing on the truck top, he hooked a ring to the control cable attached to the finished storage bin slide gate discharge valve and began pulling on the cable to open the valve. When the valve was approximately one-half open, the swivel pulley through which the control cable works became loose from the anchoring device and threw the injured employee off balance, causing him to fall backwards to the top of the truck and then to the ground.

Cause: 1. The anchoring device for the swivel pulley through which the slide gate valve is guided worked loose.

2. The footing on the hopper truck was not secure because of the rounded roof.

3. Originally, this loading location was used for loading hopper railroad cars which are three feet higher than loading trucks and there are inadequate platforms provided for truck loading.

Preventive Measures: A study is being made which, when completed, will provide for a safe loading platform for this area. In the meantime, employees loading trucks will wear safety harness attached to a cable strung the length of the loading bins.

CASE HISTORY NO. 607

Phenol Burns

Description: A chemical operator received phenol burns and scald to face, neck, and left arm when draining the water wash from the dehydration column.

The dehydration still had been shut down from normal operation and the sump of the column was being cleaned by circulating about 300 gallons of hot water through the column. When the washing had been completed, it was necessary to discharge the washing to a catch pit. After closing valves on the delivery side of inlet of the pump, the injured removed a 1-1/2-inch plug from the base of the pump. He then opened a six-inch valve on the inlet to pump from the base of the column. The hot liquor, about 90°C., flowed freely from the plug opening and flowed on the catch tray of the pump and splashed upwards on to his face, neck and left arm. He was working alone on this operation and he was wearing spectable type goggles and P.V.C. gloves.

The dehydration column had been working some time ago without the addition of copper oxide which he now used in the column. The pump inlet line had a half-inch drain valve but it had been found that since using copper oxide in the column this drain cock was blocked with sludge so the practice of using the 1-1/2 inch drain plug at the base of the pump for draining the column sump had come into operation. The injured stated that no liquor ran from the pump when he removed the 1-1/2 inch plug. There should have drained from this plug some hot liquor as the short length of piping from the pump to the cock on delivery line would be full of liquor. It is assumed, therefore, that the plug hole was blocked with sludge. When he opened the six-inch valve on the inlet to the pump the liquor removed the sludge and the wash came out at too great a flow causing it to splash against the bottom of the catch tray and upwards causing the injury.

The side of the face, neck and left arm were burned and scalded and the injured suffered from shock. He was taken to the hospital where he soon recovered from shock and is progressing satisfactorily.

Cause: The hot liquor was run off at too fast a rate owing to the difficulty of regulating the flow through a six-inch valve.

Preventive Measures: A new 1-1/2 inch drain cock is to be fitted on the inlet to the pump. This cock is to be fitted as close as possible to the six-inch line. A steam line is to be fitted to clear the 1-1/2 cock should it be blocked with sludge. If the steam line fails to clear sludge blockage, a stabber will be fitted to do this. Written instructions will be issued for this operation of draining the column sump. Full face visor, gauntlet gloves, and full protective clothing will be worn by the operator.

CASE HISTORY NO. 608

Chlorine Leak

Description: A chlorinator operator noticed an excessive pressure on the chlorine manifold and notified the chief operator who then proceeded to the area and found the chlorine manifold pressure gauge to be reading approximately 60 psig; normal operating pressure is 20-25 psig. He observed water in the chlorine rotameter glasses and detected a chlorine odor in the area and immediately closed the chlorine valve feeding chlorine to the manifold system from the vaporizer. Upon recognizing the hazard, he instructed the operator not to go above the vaporizer to the liquid chlorine valves but to proceed to the chlorine car and close all valves. Meanwhile chlorine and steam backed up 6 to 8 feet in the liquid chlorine line as indicated by its hot, smoking appearance. Chlorine started coming freely from the steam trap lines. The chief operator sent the chlorinator operator to the Chlorine Plant to inform them of difficulties and request them to shut the plant down. The steam condensate line on the vaporizer broke off, allowing steam, chlorine, and fire to emit from the vaporizer. Gas masks were obtained for personnel in the area. The plant guard on duty was notified of the failure and was requested to call the police.

The chlorinator operator went to the highway adjacent to the plant to stop traffic. Department supervision were notified of the failure. Upon arriving in the area of the plant (approximately 4:30 a.m.), they toured the area adjacent to the plant and detected no chlorine odor. Total time of the fire was 10 to 15 minutes.

Cause: The chlorine vaporizer tubes developed a leak accelerating corrosion of the tube bundle. The chlorine and iron reacted (at approximately 482°F.). Chlorine entered the steam chest and discharged through the condensate line. The condensate line corroded off and fire shot from the vaporizer. Chlorine gas was emitted to the atmosphere.

The chlorine vaporizer had been in intermittent service since December 24, 1958. At the time of the failure, chlorine was being fed from a tank car.

Analysis of the material recovered from the gaseous chlorine line indicated no presence of organics or sulfur compounds. Material in the line assayed as wet $FeCl_3$. Inspection of the rupture disc found it intact. This indicated the pressure in the vaporizer did not exceed 225 psig.

It is the opinion of the Investigating Committee that the failure of the chlorine vaporizer was caused by the reaction of chlorine on the steel tubes accelerated by high temperature.

Preventive Measures:

1. Reduce the vaporizer steam supply pressure to 15 psig or less. Provide a pop valve in the steam system to insure this pressure is not exceeded.

2. Use heavier gauge tubes to allow for corrosion.

3. Periodically inspect the vaporizer tubes for thickness - inspect every six months (first inspection to be made after three months).

4. Install a conductivity meter with alarm in the condensate line to signal when the condensate contains chlorine, if practical.

5. Before putting the vaporizer back in service, hydrostatically test both the tube and shell side to 225 psig and 375 psig, respectively.

CASE HISTORY NO. 609

Catalyst Tower Ruptures

Description: At approximately 4:00 a.m., a 3 x 30 ft. catalyst tower in a hydrocarbon stream ruptured and threw flaming catalyst some 1500 feet. The ruptured tower burned fiercely for half an hour. Fortunately, the explosion force was directed away from any occupied area and therefore no one was injured.

Cause: Due to the failure of a flow ratio controller, excess hydrogen was entering the vessel prior to the explosion. The excess hydrogen caused "hot spots" to develop in the catalyst bed, and the resulting rapid thermal decomposition of the gas stream ruptured the tower.

Preventive Measures: Hydrogen flow regulating system is to be improved by installing warning devices and automatic shutoff of hydrogen flow if "hot spots" develop in the catalyst bed of the tower.

This improved system will divert gas stream to a stand-by catalyst tower if any "hot spots" do exist.

CASE HISTORY NO. 610

Static Ignition

Description: An employee had siphoned 55 gallons of dioxane from a grounded drum into a reactor through a polyethylene tube. A piece of gauze had been attached by means of wire to the end of the tube to act as a filter. When the siphoning was finished and the operator withdrew the tube, the vapors exploded within the drum. Flames issued from the bung and burned the operator about the face, neck and arms. Safety glasses protected the operator's eyes from being burned.

Cause: A static spark was generated either by the flow of liquid and air through the tube or from sliding the tube through the operator's rubber glove as he withdrew it.

Preventive Measures: The drum and reactor will be bonded by a static wire. The filter gauze will be secured by string instead of wire. Operators should be cautioned against drawing the tube through their rubber gloves.

The Physics Department is investigating some of the aspects in relation to the generation of static by passing fluid through the wire gauze.

CASE HISTORY NO. 611

Oil Vapor Explosion

Description: During the start-up of a "mud" roaster oil burner, an employee was experiencing some difficulty in igniting it. A fellow employee came to give him assistance by holding an igniter (an oil soaked rag on a long rod) through an open porthole while the operator attempted to control the flow of oil to the burner. The combustion air valve was discovered to be closed and as the operator opened it, the oil vapors ignited violently and burned the man holding the igniter. Safety glasses definitely saved the burned man's eyes from injury.

Cause: Since the "mud" roaster was warm the oil vapors were heated above their flash point. When the combustion air and warm oil vapors mixed, an explosive concentration was formed and they were ignited by the oil soaked igniter.

Preventive Measures:

1. Remote controls and automatic igniters will be provided for igniting the oil burners.
2. The operating procedure will be rewritten and a step-by-step checkoff sheet will be part of the procedure for lighting the burners.

CASE HISTORY NO. 612

Waste Solvent Fire

Description: Waste solvents are fired through two steam atomizing oil burners into the secondary "combustion chamber" of a large incinerator. This incinerator is of a type designed for municipal use and consists of a furnace charged from the top through a large hopper with a power operated sliding gate. A hoist operator at the top level uses a clamshell bucket on a monorail hoist to feed the charging hopper.

Products of combustion from the top of a primary furnace are led to a secondary combustion chamber, downwards through this vertical cylindrical chamber and thence through a spray chamber into the stack.

Waste solvents are fired through the burners when combustion chamber temperature is over 1400°F. Waste solvent pumps are interlocked with temperature control so that solvent cannot be pumped when the temperature is below 1400°F.

Miscellaneous chemical wastes and other difficult waste products are placed in fiber drums which are dumped, one at a time, into the combustion chamber by a remote operated charging hopper in the side of the chamber. These burners and chemical waste hopper are at the second floor level of the building; ash removal is at the first floor level.

Due to the nature of the contaminated waste solvents, the armored metal hose to the burners often becomes clogged. When this happens, operators close a 1/2-inch gate valve, disconnect the line at the burner and blow it out into one of the chemical waste drums.

After blowing out a burner line and while the operator was reconnecting it, the 1/2-inch gate valve broke away from the 1/2-inch pipe nipple to which it was attached. Escaping solvent sprayed the operator who immediately got under a safety shower behind the barrier for the chemical waste hopper. He apparently pressed the stop button of the solvent pump as he did so.

Solvent vapor ignited and while he put out fire in the front of his clothing, heat and flame forced him to run down the open stairs to the first floor level where he pulled a second safety shower and extinguished the fire except for smoldering. He then ran to a nearby medical station.

A helper nearby was involved in the flash fire, apparently became confused and ran upstairs to an open grating mezzanine level from which point he was rescued by plant firemen.

The charging operator at the top level escaped over the roof without trouble.

A plant fireman collapsed, and has heart involvement as well as difficulty due to smoke inhalation. A second fireman also had temporary difficulty from smoke.

Self-contained breathing apparatus is used regularly but firemen did not stop to put on this equipment because of the need for extreme speed in the rescue operation.

The two operators received first and second degree burns of appreciable area and a lesser extent of third degree burns.

Cause: The proximate cause of this fire was the breaking of a 1/2-inch standard weight, threaded fitting. Replacement will be not smaller than one inch, extra heavy including the gate valve. A permanently connected arrangement will be made for blowing out lines with air pressure into the combustion chamber, making use of three-way valves. This system will be electrically interlocked with the waste solvent pump so that both burners will be shut down when blowing lines.

CASE HISTORY NO. 613

Static Discharge from Worker's Clothing Ignites Carbon Bisulfide Vapor

Description:

1. Injured employee was dismantling an outlet pipe connected from a barometric condenser to a Stokes dryer which was located on a mezzanine floor.
2. He loosened the outlet pipe nipple with a wrench enough to unscrew the nipple by hand. Just when his hand touched the nipple, an explosion and fire occurred in the barometric condenser which contained some residual carbon bisulfide vapors.
3. The employee, attempting to get away from the area, climbed through a railing and started climbing down some piping. As he was doing so, he slipped and fell to the ground sixteen feet below, injuring his arm.

Cause:

1. Employee was wearing clothing of synthetic fibres which probably built up a static electrical charge. The electricity discharged when the employee touched the nipple, which probably ignited the residual carbon bisulfide vapors remaining in the condenser.
2. Since carbon bisulfide containers are difficult to decontaminate with water, the condenser should have been blanketed with inert gas, or completely steam cleaned.

Preventive Measures:

1. Vessels will henceforth be blanketed with inert gas when there are similar exposures, and employees will wear air masks for protection from possible inert gas exposure.
2. Wearing of static-electricity generating clothing by employees has been prohibited on jobs of this nature.
3. Wearing of shoes with conductive soles is being investigated for possible use on future similar jobs, and will be made available to employees when required.

CASE HISTORY NO. 614

Industrial Truck Fire

Description: The truck involved in this fire was a Hyster Model HC-50 and was being used in connection with a Blast Furnace operation removing furnace slag in a pot. The furnace had been tapped and the pot was filled with slag to the normal level. During this filling process the pot was suspended to the proper height by the Hyster truck. When the pot was filled, the truck backed away from the furnace, had stopped and was ready to proceed in a forward direction to take the slag to the dump. While the truck was stopped, the load dropped, spilling molten slag which flowed under the truck. Fire ensued immediately under the truck and the operator jumped to safety and was not injured. The Fire Department was called and the fire extinguished.

Cause: Subsequent investigation revealed that a hydraulic oil connection under the truck leaked which evidently caused the load to drop. The molten slag obviously set fire to the oil that had leaked out. The intense heat of the molten slag and ensuing fire also burned off the hydraulic rubber hose connections, adding more oil and rubber fuel to the existing fire. The resulting damage to the truck was approximately $800.00

Preventive Measures: It is possible that a preventive maintenance inspection could have caught the loose connection and prevented this incident.

CASE HISTORY NO. 615

Dump Truck Fatality

Description: A Dempster-Dumpster truck driver drove to the dump with a box load of waste material. He went under the suspended Dempster box, which was open, apparently to loosen remaining waste material. At this time the locking device failed, and the main bucket body fell, trapping him between the two bucket sections.

The employee, who was fatally injured, was found pinned between the drop bottom and the main body of the eight cubic yard Dempster box.

Cause:

1. Investigation disclosed that the latching device was apparently not completely engaged during the dumping operation. The spring mechanism, which positions the latching hook, failed to provide adequate tension for positive hook-up to bucket lifting bar.
2. Employee being under suspended bucket.
3. Use of faulty equipment.

Preventive Measures:

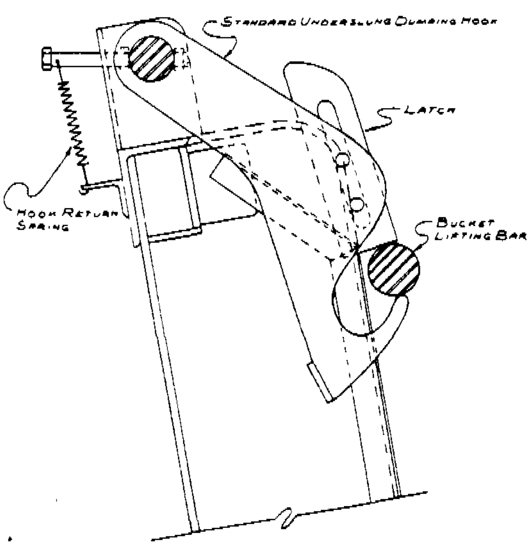
1. The dumping hook and spring mechanism will be replaced with a newly designed type. (See illustrations.)
2. Employees will be instructed never to position themselves under a suspended object, and warning signs to this effect will be placed on all buckets.
3. All supervisors will be instructed to review this incident with their personnel to emphasize the importance of reporting defective equipment.

CASE HISTORY NO. 616

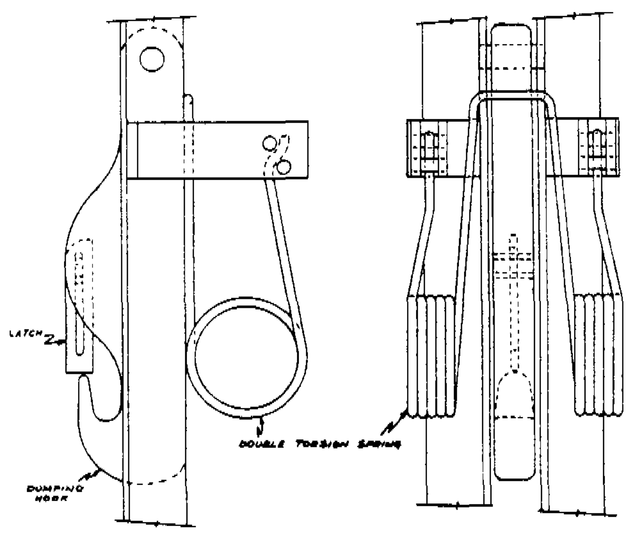
Explosion--Ether Vacuum Distillation

Description: An ether solution of a steroid intermediate resulting from a grignard reaction, is quenched in dilute HCl and washed with water. The ether solution is then pumped to a still and vacuum concentrated. A reciprocating type vacuum pump is used for this concentration step and is provided with an after-cooler and receiver to recover ether vapors.

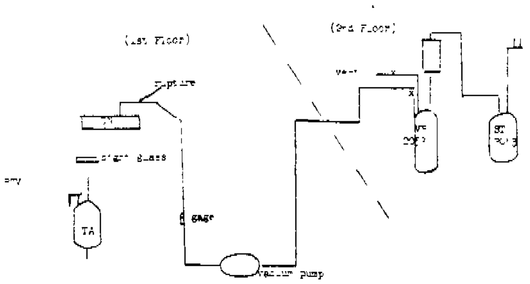
On this particular batch the operator started the vacuum pump which is in a first floor pump room and the pressure began to drop normally.



Type of hook and spring involved in accident.



Newly designed spring and hook



He returned to the vessels on the second floor and opened the valve on the vacuum line from VR2053 but failed to close the adjacent valve on the vent line. After 2 or 3 minutes he noticed that there was only 10 inches of vacuum. At the same time a loud report was heard. The operator and supervisor shut the vacuum valve at the vessel and then went to the pump room. Vapors of isopropanol were dense. The vacuum pump then was shut off.

Investigation: An investigation revealed that an eight inch long horizontal pipe nipple (2 inch diameter carbon steel) on the discharge line from the vacuum pump (see diagram) had been blown out of the line. It was found in two pieces both of which were almost flat. The pipe broke at the factory seam and in a ragged pattern at another section. A small irregular section about 1-1/2 x 1 inch was not found but fitted into the latter area. In addition, a water line to the after condenser was broken. No one was injured and there was no other damage. The investigation also revealed the following:

1. The after condenser was not plugged.

2. A pressure relief valve on the after receiver had apparently not functioned.

3. The pressure gauge in the discharge line had indication of off scale (over 60 psi) pressure, however, the Bourdon tube was not ruptured.

4. A piece of pipe from the discharge line (presumed to be in the same condition as the piece that exploded) was removed and subjected to a pressure of over 4500 psi with no effect.

5. The flame arrestor on the receiver vent line appeared to be slightly obstructed, but not unusually so. The vent line itself was neither plugged or obstructed.

6. There was no apparent physical distortion of any line or vessel except the nipple which was torn apart and flattened.

7. A negative test for peroxides was obtained on material taken from: the after receiver, the condenser, the primary receiver, and pump suction and discharge lines.

8. Distillates from subsequent distillation were tested for peroxides. The tests were negative.

9. There was no evidence of smoke or combustion.

10. The appearance of the nipple indicated a detonation had occurred rather than ordinary rapid combustion or explosion.

11. Isopropanol vapors were present since the previous operation was the charging of isopropanol by vacuum to the previous batch.

12. Spectrographic analysis of scrapings from the pipe which exploded and another adjoining section did not reveal any significant contamination present.

Conclusions: The exact cause of this explosion has not been determined but two theoretical causes are postulated.

1. Peroxide Detonation

Under certain conditions ethyl ether can fix oxygen from the air to form peroxides. Most of these peroxides are shock sensitive when dry and are easily detonated. The piece of pipe which shattered was horizontal and was pitted. It is conceivable that some ether remained in the pipe from the previous distillation, that peroxides formed, were left as a residue and detonated as a result of the pump vibration. Although the pump is normally a very quiet running pump, it was probably pounding due to overload at the time of explosion.

2. Vapor-Air Detonation

Recent literature - (Beware Detonations - Chemical Engineering - January 11, 1960) describes detonations of vapor-air mixtures, with points of localized pressure of over 12,000 psi, demonstrating results similar to this occurrence. The source of ignition in our case, however, has not been determined.

Preventive Measures: Research as to the cause of this explosion is continuing. A vacuum steam jet was substituted for the vacuum pump before the operation was resumed.

CASE HISTORY NO. 617

Leaking Settler Tank Causes Fire

Description: Difficulty had been experienced with the settler tank in a Research Building leaking solution on the floor of the deck containing the mixer-settler equipment. The leaking tank was taken out of service for necessary repairs.

Preparatory to cleaning the spillage, an electrical control panel was covered with plastic sheeting, and an electrician was instructed to remove the power in this area. Shortly after the equipment operator had begun the washing-down operation, it was noted that there was some arcing from the condulet along the wall one floor down. The washing was stopped, and at this time flames were noted shooting upward. The fire was extinguished by the use of a CO_2 extinguisher. The arcing began again, however, and after the contents of a second extinguisher were exhausted the entire wall suddenly burst into flames. The operator, seeing that the fire was out of control, left the building and notified the plant Fire Department.

Supervisory personnel and another electrician were summoned, and after the power and utilities to the building had been shut off, the fire was quickly brought under control by the plant and city Fire Departments. Most of the damage to the building and contents was confined to the upper decks. There were no personal injuries.

Cause: After an investigation, it was concluded that the fire resulted from washing solutions containing hexone off the deck and down the south wall. Apparently the solution entered the condulet and caused the arcing. The switch controlling the power in this circuit had not been pulled and the power was still on the circuit.

Preventive Measures: Instructions were issued to the effect that the working areas be sprinkled and that adequate ventilation for the removal of flammable vapors be provided. In addition, better drainage was to be supplied to the mixer-settler area.

Additional training was given to operators as to the location of utility control valves and electrical switches. Building and shift foremen were asked to make themselves thoroughly familiar with the controls in their own building and have knowledge of where controls are located for other buildings in the immediate area. A flow diagram of the location of utilities and electrical controls for all buildings was prepared and made available.

CASE HISTORY NO. 618

Dust Cloud Ignites--Fatal Injury

Description: A machine operator received severe body burns which later proved to be fatal, when a dust cloud ignited. A machine operator was in the process of unloading a two-foot conical ball mill containing micron-sized titanium carbide. Approximately 95% of the product was removed from the mill. It was then being rotated in order to completely clean it when a dust cloud ignited, setting the operator's clothes aflame. He received severe body burns which later proved to be fatal.

Cause: The product had been milled to a finer size than desired. The dust cloud could have been ignited by a lighted cigarette or other causes.

Preventive Measures:

1. Prohibit the milling of reactive materials to micron size until approval, based on results of pyrophoric evaluations, and the means of performing the work in an inert atmosphere to prevent oxidation is established.
2. Written instructions relating to the milling procedure to be followed should be sent to the foreman of the processing department to avoid possible procedure errors.

CASE HISTORY NO. 619

Line Maintenance

Description: An employee was helping to remove a blind flange from an acid line. The residual pressure in the line sprayed acid into his face, which resulted in chemical burns to the face and eyes. The employee was wearing safety glasses, which helped to minimize the eye burns.

Cause: There was a residual pressure on the pipe line, unknown to the employee. Upon opening the line, this pressure sprayed the acid onto the employee. It was assumed that this line had been drained and all pressure relieved.

Preventive Measures: All employees will be required to wear a face shield or chemical worker's goggles when opening lines that have contained hazardous chemicals.

The importance of treating all pipe lines as though they were under pressure will be stressed to all employees.

CASE HISTORY NO. 620

Autoclave Explosion--Fatal Injuries

Description: The sodium salt of trichlorophenol is manufactured in an autoclave. The autoclave is charged with sodium hydroxide, methanol and tetrachlorobenzene. The mixture is heated with agitation. The peak operating pressure is approximately 400 pounds.

On the day of the accident the vessel had been charged and was in the process of heating up when the pressure and temperature increased rapidly and an explosion ensued. Fatal injuries resulted.

Cause: The cause is unknown. The autoclave was equipped with a rupture disc set to relieve at 660 pounds at 70°F. The rupture disc was followed by a relief valve in the same line set to relieve at 550 pounds pressure. These safety devices worked as they should have. It is estimated that 7 to 8 seconds elapsed between the time of the rupture disc failure and the explosion. We believe the explosion was due to the very high pressures blowing off a 6-inch nozzle from the vessel, thus liberating vaporized methanol into the immediate area, and that possible sparks from this nozzle striking a wall caused the methanol vapor to explode.

The autoclave was fabricated according to ASME Code for Unfired Pressure Vessels, Section VIII, 1950 edition. The vessel was designed for a working pressure of 650 psig and with a capacity of 1250 gallons. It was constructed of ASTM A285 grade C flange quality steel and was x-rayed and stress relieved. It was equipped with an agitator driven by a Class I, Group D explosion-proof motor. This vessel was inspected in August of 1959 and found to be satisfactory in every respect.

Possible causes are:

1. The inclusion of foreign substances which would accelerate a reaction or cause it to react in a different manner. We have investigated this possibility and, to the best of our knowledge, find nothing unusual in the particular raw materials on hand.

2. Since all the raw materials are charged at once, the reaction, if it gets out of hand, can proceed until it consumes the raw materials present.

Preventive Measures: The action being taken to prevent a re-occurrence of such an incident is as follows:

1. We will continue to monitor raw materials received as we have done in the past.

2. We will design a much stronger vessel and equip it with greatly oversized relief devices. This vessel will also be isolated by a concrete wall built around the three sides of the vessel contiguous to other operation. Controls will be placed outside of this wall.

3. We will add one of the reactants continuously so that its concentration is at no time sufficient to react with all of the materials in the vessel.

Editor's Note: The following has been received from Geigy-Werke Schweizerhalle A.G. of Switzerland, regarding case history number 620, "Autoclave Explosion--Fatal Injuries".

"Since we have knowledge of a report on an almost identical accident which happened in a German plant not belonging to our organization, we would like to pass the information on to you without being able to certify its exactness. The intention being a possible contribution to find the true cause and to draw attention to potential health hazards.

The manufacturing procedure is exactly the same: Autoclave is charged with sodium hydroxide, methanol and tetrachlorobenzene. The normal operating temperature should not exceed 125 degrees centigrade in the phase of distillation of excessive methanol. It happened one day that the temperature rose quite unexpectedly to about 400 degrees centigrade. At that moment vapours escaped through the safety valve leaving a carbonized residue within the vessel. After ten days the entire personnel of the shed reported ill, (50 persons), and all suffered from more or less severe liver damage. Some of the lesions were irreparable and some others healed very slowly within 3 years. It was thought that a spontaneous decomposition took place and pentachloro-oxy-diphenyloxide was formed. This substance seems to be extremely toxic, very sticky, and considerable time was spent in cleaning after the accident.

Similar incidents are reported to have happened when byproducts from the manufacturing of gamma-hexachlorocyclohexane were treated."

CASE HISTORY NO. 621

Fork Truck Accident

Description: A grab arm type fork truck being used to load a trailer "dropped" in No. 2 truck bay. As it rode onto the loading plate and its front wheels entered the trailer, the trailer rolled out 1 to 2 feet and stopped. The fork truck operator, when he realized this, left the truck and scrambled back to the platform. Before any further measures could be taken, the trailer rolled out further and the fork truck dropped down into the bay. Fortunately no one was hurt and there was only slight damage to the fork truck and repair was made the following day.

Preventive Measures:

1. Driver dropping trailer must have air hoses connected to trailer which will lock trailer wheels.

2. Shipping clerk must check trailer immediately before loading to make sure rear trailer wheels are properly chocked.

3. Fork truck driver must check independently to see if trailer wheels are properly chocked.

4. Owner of outside trailers has agreed to step "1" and the unit will be inspected before they back in to make sure this is done.

5. Any shipping clerk and/or fork truck driver failing to abide by these safety precautions shall have the following work day off without pay!

CASE HISTORY NO. 622

Explosion--Maleic Anhydride

Description: On January 9, 1960, a vessel containing partially solidified maleic anhydride exploded violently. The explosion injured five operators. Two of the men died of injuries and burns a few hours after the accident. Damage to plant facilities in the blast area amounted to about $250,000. The damage resulted primarily from the force of the explosion and not by fire.

The vessel which exploded was of Type 304 stainless steel construction, fully insulated, and had a capacity of 800 gallons. The diameter was 4 ft. 6 in., shell length was 6 ft. 0 in., shell thickness was 1/4-inch, thickness of heads was 5/16-inch, and the vessel was designed for 100 psig pressure or full vacuum and a maximum temperature of 250°F. One 2-inch by 3-inch relief valve was set at 90 psig. This valve had functioned properly prior to the explosion, but was inadequate in size to cope with the volume of gas evolved.

Cause: An extensive investigation into the cause of the accident has revealed that the explosion was caused by decomposition of maleic anhydride, catalyzed by sodium ion (in the form of caustic) and heat (300°F or more). Sodium introduced as sodium hydroxide or other sodium compounds into maleic anhydride causes an exothermic decomposition which rapidly produces large volumes of gas (carbon dioxide). This reaction was generally unknown at the time of the explosion.

The vessel was connected with a process unit which was periodically cleaned with a weak caustic solution. Since the vessel contained maleic anhydride, top and bottom valves had been closed so that the caustic solution could not enter the vessel while other parts of the processing unit were being chemically cleaned with this material. However, sodium was found in samples from both sides of the valve at the bottom of the vessel and also in a sample taken from the seat of this bottom valve. It is concluded that at some time prior to the explosion the bottom valve had been open enough to allow the caustic cleaning solution to enter into the vessel. This could have happened several hours prior to the explosion, or perhaps a few minutes prior to the explosion. The heat evolved by the neutralization of the maleic anhydride with the caustic, and heat which possibly may have been supplied by steam, raised the temperature to a point where the sodium ion-induced decomposition of maleic anhydride further increased the temperature. Since the vessel was insulated, very little heat was lost. Once the decomposition started, the heat released from this exothermic reaction caused an autocatalytic runaway decomposition which could be described as a thermal explosion. Large amounts of carbon dioxide gas were liberated which built up the pressure in the vessel very rapidly. The rate of gas evolution was too rapid for the relief valve to handle completely, and the pressure increased beyond the bursting point of the vessel. It is believed that the gas pressure from this thermal explosion ruptured the vessel.

It has been found as a result of the investigation following the explosion that other alkali and alkaline earth compounds, such as potassium. lithium, calcium, barium and magnesium compounds, may also bring about the decomposition of maleic anhydride. It was found that amines and other nitrogen compounds also will trigger the decomposition of maleic anhydride.

Preventive Measures: In order to prevent future accidents of this nature, caustic cleaning solutions and other alkali compounds and amines have been prohibited for use in equipment in maleic anhydride service. The replacement vessel has been redesigned and has been equipped with improved warning devices and also larger pressure relief facilities.

CASE HISTORY NO. 623

Chlorine Exposure

Description: On January 19, 1960, a section of 200 psig steam header was blocked in for maintenance work. A tap from this section of header reduces the steam to 12 psig for use in heating a chlorine header. Since this section of header was blocked in making no steam available for chlorine heating, the chief engineer closed the chlorine feed regulator at the chlorinator.

After completion of the maintenance work on the 200 psig system the header was warmed up. Shortly thereafter the chief engineer smelled chlorine in the chlorinator room and blocked in the chlorine supply line just outside the door. About 45 minutes later, an operator reported to the chief engineer that he smelled chlorine outside the chlorinator room. The chief engineer, believing that the one chlorine valve which he had closed must be leaking, closed the second valve in the system. A few minutes later, the diaphragm type pressure gauge blew off, allowing chlorine to issue from the 3/16-in. orifice in the lower portion of the pressure gauge. The chief engineer, a boilermaker, an adjacent area chief operator and supervisor inhaled chlorine gas. All four men were treated in the dispensary and three of these were sent to the medical clinic for examination. All were released shortly thereafter.

Cause: Liquid chlorine was trapped in the system between the closed block valves. When steam entered the chlorine heater, a vapor pressure exceeding the maximum pressure of the gauge (150 psig) was exerted on the system and caused the gauge to rupture.

Preventive Measures:

1. Repairs were made to the system and new 0-300 pressure gauges were installed in place of the damaged ones.

2. An Engineering Work Order has been initiated for study of the chlorine system in the power departments with special instructions on pressure control, pressure relieving facilities and chlorine heating control.

3. This incident is to be used in safety meetings to emphasize the proper handling of chlorine and written instructions will be developed and incorporated into the department's operating manual.

CASE HISTORY NO. 624

Valve Repair Men Injured

Description: Two men were assigned the job of repairing a 3-way valve. They were advised by their foreman that it was leaking internally. They checked with the Biphenyl operator about pumping the product from the high boiler catch tank and, when advised that there would be no transfer, physically checked the pump and valves, and found the pump off and valves closed. They then proceeded to the 3-way valve located at the southeast corner second level of the department. External adjustments were made to the valve to stop leaking. The operator entered the area and was called to the job site and asked if the line was okay. The operator indicated that he was not pumping through the line. The valve packing gland was then removed and the packing checked. The packing was found to be in good condition and the pipefitter started to replace the gland. At this instant there was a sudden discharge of hot product.

Both pipefitters were sprayed about the head and shoulders and suffered face and neck burns. The product sprayed out for a very short period of time (seconds) in an umbrella effect. The fact that they both wore safety goggles undoubtedly prevented the incident from being more serious. The men were taken to the dispensary by their foreman and given emergency treatment.

Cause: There were two contributing causes for the accident:

1. Lack of complete communication in establishing the scope of the work.

2. The location of valve in the lowest section of a series of transfer lines.

The liquid material that sprayed the area was apparently contained in a vertical section of 2-in. pipe, 4 feet high, immediately west of the 3-way valve. The material was suddenly released when the valve plug or packing moved.

The plant tagging procedure was not used, although personnel involved physically checked pumps and valves to determine whether they were in a safe position.

Preventive Measures: The Committee recommends immediate action on the following:

1. Maintenance and Production personnel be made fully aware of the complete scope of every job, thereby enabling every man to fully evaluate all the potential hazards involved in a job.

2. Install drain lines with flanged gate valves on the east and west process lines at the 3-way valve.

3. The Maintenance procedure for working on a valve located in a trapped section of line shall be:

   The mechanic will wear a face shield and chemical goggles, break the flange closest to the valve using the standard safe method, i.e., open the flange away from himself.

4. All plant personnel should be re-instructed within the next two weeks on the use of the plant safety tag-out procedure.

Secondary — Investigate the process piping system centered at the 3-way valve and determine the possibility of simplifying transfer operations.

Superintendents will report status of recommendations to the Plant Manager bi-monthly, with copies to the Investigating Committee, until all phases of recommendations have been completed.

CASE HISTORY NO. 625

Vinyl Chloride--Laboratory Accident

Description: The employee was disposing of excess vinyl chloride sample quantities by discharging the material into the air stream of a conventional bench type laboratory hood. The sample containers are stainless steel tanks, round end—about 4 x 6 inches. Connections are provided at each end to facilitate filling. The residual quantity usually amounts to from 200 to 400 cc. and at ambient laboratory temperature has a vapor pressure of about 60 psi.

One such sample container had been inverted in a ring stand at the right side of the hood and the valve "cracked" to allow the vinyl chloride to drip into a beaker for evaporation. A two liter open-top Dewar cooling bath containing dry ice and isopropanol stood at the left. A sheet lead pan covered most of the bottom of the hood. The employee held a second sample in one hand, sloped the outlet downward and opened the valve, discharging VCl as a vapor-liquid spray onto the bottom of the hood. Within 5 to 10 seconds the vapors in the hood ignited and for a short period the upper half of the employee's body was enveloped in flames.

At this point the injured dropped the container to the bottom of the hood and retreated from the room. He was wearing a short sleeved shirt and the arm burns extended above the elbows. His face was burned but his eyes were protected by safety spectacles. His cotton work clothing did not catch fire nor was it scorched.

The injured then walked 60 feet down the hall to the lunch room to tell fellow employees of the fire and that he had sustained burns. He then went to the change room, 50 feet, to rinse his face and arms. Meanwhile the fellow employees summoned assistance which arrived within 5 minutes. The fire alarm system was not activated.

(Security personnel transported the injured to Medical immediately for treatment and subsequently to the City General Hospital by car where he was confined for one month under treatment by his personal physician.)

The fire in the laboratory room (door closed) continued unabated and undisturbed as the employees had heard two dull thuds issue from the fire area, perhaps two to three minutes apart, and did not wish to chance entering the room. These reports came from rupture of the stainless steel sample containers that were in the hood. The two containers "tore" into several pieces each, possibly indicating an accelerated rise to the area of or above the critical pressure (775# at critical temperature of 317°F) of vinyl chloride. These pieces were thrown across and around the laboratory room and produced some damage.

When the fire subsided, extinguishment was accomplished by the use of one 20# extinguisher.

Cause: There are no electrical service connections in this hood and the hood contained no electrical equipment. The overhead light in the hood was protected by a "vapor-proof" globe but this was intact before the fire--the switch is external. The employee reports that while discharging a sample in the same manner about one-half hour previously he noted a "tickle" in the palm of the hand holding the container, indicating a static discharge. He had never noted such an event and attached no importance to the incident. Such was not noted at the time of the accident but static appears to be the most reasonable ignition source.

It has since been established that a "fogging" discharge of vinyl chloride from such a container is capable of building a static charge of consequence. True gaseous discharge did not produce a charge that was measurable with the equipment available.

Preventive Measures:

1. All Control Laboratory employees have seen the USBM-AGA film on static electricity.
2. Flammables are being disposed of in open air with static grounds as needed.
3. Special disposal facilities are to be provided.
4. In laboratory quantities of flammables are being held to an absolute minimum.
5. Long sleeves specified.
6. Hood ventilation being studied.
7. Eye protection re-emphasized.
8. Sampling methods under study.
9. Problem of sample container pressure relief being studied.

CASE HISTORY NO. 626

Chemical and Thermal Burns

Description: A phenolic kettle operator opened the #3 kettle manhole during a class A cleanup and thereby permitted 100°C caustic solution (3-5%) to boil over from the open vessel. Second degree burns were sustained on both legs (below the knees). Immediate flushing with water and medical treatment permitted the employee to return to work without loss of time.

According to standard practice a class A cleanup of the #3 phenolic kettle was initiated following the last of a series of 497 Varnish batches. This cleanup was started shortly after lunch on the day of the injury. A class A cleanup involves filling the kettle 2/3 full (approximately 2000 gal.) of cold water, introducing 600-1000 pounds of 50 per cent caustic by applying vacuum to the kettle, venting the kettle to atmospheric pressure, application of steam to the kettle jacket and holding the kettle contents at 100°C for an hour. Normally the caustic solution is then cooled to 80°C, pumped to the hold tanks and then discharged to the sewer. In this case, however, supervision had instructed operating personnel to backflush the condenser prior to transferring the wash caustic to the hold tanks. Condenser backflushing is not a routine operation and is performed only when supervision determines that it is necessary. Backflushing is accomplished by circulating the hot caustic solution through a portion of the varnish transfer line and pump, then through a temporary rubber hose section which joins the varnish transfer piping and the kettle vent line (on discharge side of condenser), then back through the condenser into the kettle. The temporary connection to the vent line leads to a closed system when the necessary steam jet and transfer line valves are blocked.

At the time of the accident, one hose section had been attached to vent line and another to the varnish packout line. The two hose sections were not as yet connected. The injured had backflushed a condenser once before and was depending on his past experience plus verbal comments passed on by other operators on how best to proceed.

He recalled a conversation with another operator who had noted that before starting the circulating pump it was necessary to open the manhole to avoid a pressure build-up during the backflushing. He recalls performing the following sequential steps immediately prior to the accident.

1. Steam to jacket turned off but jacket not vented. Instrument charts shows 30 psig steam.
2. Within 30 seconds he loosened manhole and started to swing open.
3. As soon as manhole was lifted, hot (100°C) caustic solution boiled out, striking the employee at knee level.
4. At this point, the injured dropped the manhole cover and dashed for the nearest shower.

After flushing with considerable water, the employee reported to the infirmary and was immediately taken to the company physician and treated for second degree burns on both legs.

Cause: The investigating committee discussed the accident with the injured employee, and other operating personnel. In addition, the various temperature-pressure instrument sheets were analyzed.

The committee has concluded that the kettle was under a slight positive pressure (1-2 psig) at the time the kettle manhole was loosened. In addition, since steam pressure was still on the jacket, the wash-solution was slightly superheated. Upon opening the manhole cover, the wash solution boiled vigorously and splashed out of the open manhole.

The committee is of the opinion that three factors led to the accident. These are as follows:

1. The fouled condenser led to the pressure build-up in the kettle.
2. Lack of a specific procedure to cover this type of operation.
3. Vent facilities are not provided which are independent of condenser and thereby are subject to plugging.

Recommendations: 1. Clean condenser.

2. Install kettle vent line off inlet condenser head.
3. Prepare detailed procedure covering backflushing operation.
4. Discontinue use of temporary rubber hoses for handling hot caustic solution. Install a permanent line.

CASE HISTORY NO. 627

Polyethylene Liner--Static Ignition

Description: An operator was pouring trichlorophenyl hydrazine from a polyethylene bag inside a fibre drum into a reactor containing methyl alcohol. As the material was emptied from the bag, the operator pulled the bag from the fibre drum and tried to shake the last bits of the chemical into the kettle. The fibre drum had a metal rim around the mouth. It is believed that the pouring of the solid or the pulling of the polyethylene bag created a static charge and the metal rim or the man acted as a condenser which discharged to the manhole on the reactor. The spark then ignited the methyl alcohol vapors in that vicinity causing a flash of fire to be issued from the manhole. The operator was burned about the face and neck.

The operator was wearing laboratory clothing consisting of a jacket, overalls, rubber gloves, safety glasses, shoes and rubbers. The glasses saved the operator's eyes from injury.

The Lesson: Static is more prevalent during the winter because cold air which comes in from outdoors is warmed up and the relative humidity is thereby decreased. However, static is also produced under other conditions. Experience shows that static is more prevalent under conditions of low humidity. Therefore, it would be wiser to discuss conditions which make static discharges possible rather than to try to enumerate all the methods of static production. Then, the reader may be able to analyze his operation and take steps to prevent the accumulation of the charges.

In order to generate a static discharge, three essentials are required. They are:

A. A nonconductor to generate a charge--plastics, liquids, clothing, etc.

B. A condenser, which will hold the charge--ungrounded metal, persons, etc.

C. A ground or a conductor of sufficient capacity and of different potential--piping, equipment, drums, etc.

As the three items come together in the sequence above, a static discharge may result.

Static electricity is generated by contact and separation of two dissimilar substances, such as a belt moving away from a pulley, paper, film, and cloth passing over rolls in a machine, etc. Static is produced when nonconducting liquids flow through pipes or hose, when they pass through the air in droplets or spray, when they are splashed, stirred or sloshed in tanks or when air or other gases bubble through the liquid. Gases passing through a nozzle at high velocity may generate static charges particularly when accompanied by droplets, spray or solid particles. Static is also generated by solid particles when they flow through pipes or slide across surfaces.

The generation of static electricity is difficult to avoid but, the dangerous accumulation of it can be avoided. Bonding, grounding, humidification, ionization or combinations of these methods are recommended where static is a fire hazard or an inconvenience to personnel.

CASE HISTORY NO. 628

Implosion Due to Defective Switch

Description: During a start-up of a pilot plant in a process laboratory, a vessel imploded because of excessive vacuum on the suction line of a compressor system. A switch installed to prevent such an accident did not function.

Under normal conditions a mixture of gases is transferred from a gas holder via a suction line, through a surge tank and into the compressor. The mixture is compressed and introduced into the reactor. Pressure in the suction line is held at 3 to 5 inches of water and a diaphragm-operated pressure control switch is set to stop the compressor should the pressure drop to two inches of water.

Cause: At the time of the start-up, a valve located in the suction line between the gas holder and compressor was closed. When the compressor was started the suction line pressure decreased, the switch failed to stop the compressor, and vacuum collapsed the surge tank and fractured a vent line. An operator stopped the compressor before further damage occurred.

The switch has been disassembled and examined. The pivot pin that supports a movable contact arm was slightly curved. This minor defect may have been responsible for the malfunction.

Preventive Measures: Personnel responsible for the operation of equipment protected by pressure controls were instructed to periodically inspect and test the performance of these controls.

CASE HISTORY NO. 629

Nitrogen in an "Air" Hose

Description: Two painters were preparing to sandblast the catalyst building elevator. One painter after getting into the sandblasting hood became dizzy and passed out before he could get the hood off. The second painter observed this and removed the hood. The man promptly recovered. It was found that the hose station to which the hood was connected was labeled "Air", but was, in fact, nitrogen. This accident could have been fatal had the man been working alone or had the job been at a high elevation.

Cause: The direct cause of this near-miss was the mislabeling of the hose station. Although it was not known when the mislabeling occurred, it was most likely that it happened during a reconstruction project in 1959. The nitrogen supply line in this building had previously been a methanol line and the color coding had not been changed. The hose station on the second floor was labeled "gas" while the hose station on the first floor had been painted green without stripes and was labeled "Air".

Preventive Measures:

1. In this particular location the nitrogen line has been properly coded and the utilities station outlets properly identified.

2. Throughout the plant a survey has been made by supervision to determine what possible hose connections are mislabeled or improperly identified, and that these be promptly corrected.

3. Emphasis will be placed in safety meetings that hose stations identification should be changed at the same time the services change, and the color coding as soon as possible after any piping revisions.

CASE HISTORY NO. 630

Sludge Frozen Valves Cause Propane Exposure

Description: An employee opened valves (3) in a line (drain leg) to drain water from the base of a propane stripping column. The drain system was plugged. The employee and a co-worker dismantled the piping up to a point between two valves. Suddenly, the propane froze the two remaining valves in the "open" position. The employee's feet were exposed to the escaping hydrocarbon stream while he was trying to shut the valves and attempting to install a pipe nipple and valve on the open line.

An additional, and more severe, hazard was the exposure of four employees to the flammable propane gas cloud while attempts were made to shut off the escaping hydrocarbon.

Cause: Presence of frozen sludge in the drain line (globe type) valves making them inoperative. Sludge was a product of acid action on the pipe iron.

Operator attempting to install pipe nipple and valve on open line against 200 pounds pressure.

Preventive Measures: Piping and valves of the drain line have been changed. Acid resistant gate valves have been used to replace globe valves.

Water will be drained twice per eight-hour shift to preclude acid concentration in the drain line. Percentage of hydrogen ion concentration readings will be taken on water drawn off from the column.

Supervision reviewed with all employees (1) the importance of depressuring equipment before attempting maintenance work and (2) the severe hazard of remaining in the area of flammable gas clouds due to possible ignition with the resultant fire and explosion.

CASE HISTORY NO. 631

Caustic Released from Pump

Description: The employee entered a unit soda tank room to lubricate pump motors. Employee states that while en route from south to north end of room, caustic soda was suddenly released from a pump about five feet away through a bleed-off line. He sustained severe caustic burns of right eye, face, lips and forehead and probable enucleation of right eye. Employee states that following the accident he attempted to stop the pump but could not. He went to the next floor level prior to flushing the burned areas with water, although an eye fountain and emergency shower were immediately available in the room.

Employee claims to have been wearing goggles (of a type not authorized for this area) but examination of the goggles immediately following the accident indicated that soda had not entered the inner area of the goggle although areas of the face normally covered by the goggles were badly burned by the 35 per cent solution of soda.

Investigation revealed a 1/4-inch plug had been removed in some manner from a pump bleed-off opening and the oil can being used by the employee was near the pump. The plug was also found near the pump. It is presumed that unapproved goggles were being worn improperly.

Cause: Eye protection inadequate. (Wearing unauthorized pair of goggles and apparently improperly.)

Preventive Measures: Establish goggle zones throughout the plant with adequate publicizing of approved goggle for the area and enforcement by supervision.

Note: Employee lost vision of right eye in a company plant accident in 1943.

CASE HISTORY NO. 632

Methyl Acetylene-propadiene Explosion

Description: An explosion occurred while handling 70-30 methyl acetylene-propadiene mixture resulting in the fatal injury of one person. Methyl acetylene has been made on a fairly limited production scale since 1955 and its hazards were investigated rather extensively, especially those relating to its ability to detonate. Tests made involved excessive shock, temperature and pressure of the methyl acetylene-propadiene mixture as a liquid in regular 119# cylinders plus high temperature tests of cylinders with vapor only. The tests showed that the liquid mixture was not shock sensitive but that a high (200°F) temperature, even in a small area, plus moderate pressures (50-55 psi.) would cause a detonation that would propagate through piping.

119# capacity methyl acetylene cylinders were being loaded by operator. Witnesses state that there was an initial flash fire followed by a muffled explosion at the immediate site of the loading station, followed by a large explosion which in turn was followed by the explosion of the methyl acetylene storage tank itself. It is felt that the initial muffled explosion was a flash of a vapor-air mixture at the loading station and that the second explosion was the detonation of the cylinder being loaded. The third and major explosion was the 6 x 20 ft. storage tank and it created real shock that shattered glass and transite in the plant proper and scattered metal to adjoining plants. It also ruptured piping from the methyl acetylene production unit and nearby storage tank. These lines were the major source of the ensuing fire.

The initial flash or explosion may have been caused from vapors from the leaking pump seal. Static or mechanical sparks or possibly the TEFC motor could have provided ignition. Also considered was the possibility that the mechanical seal on the pump could have heated due to friction and ignited the methyl acetylene. However, the pump seal did not show any undue wear on inspection.

Cause: The possible causes of the cylinder exploding were chemical contamination of the cylinder, decomposition propagating from the flash fire through the piping into the cylinder, a hot spot being formed on the piping or cylinder that caused detonation, or an air-vapor mixture in the cylinder.

The possible causes of the storage tank exploding were the decomposition propagation through the piping, puncturing of the tank with subsequent ignition and explosion, or a hot spot forming on the tank from the fire.

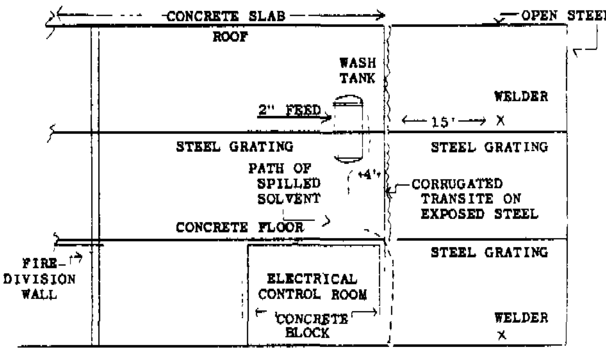
The remainder of the loaded cylinders in the immediate fire area all exploded subsequently with the exception of one that was blown clear of this area.

CASE HISTORY NO. 633

Fire Started by Welding Sparks

Description: While part of a hydrogen peroxide manufacturing process was on a scheduled shutdown, some excess equipment was being removed from an open three story section on the end of the building. Some minor changes in the supporting steel required acetylene cutting and welding; and, although plant safety regulations were being followed, sparks ignited the vapors of a volatile solvent from a small vessel overflow in the adjacent closed section of the building. The solvent had burning characteristics similar to gasoline. Before the resulting fire was brought under control about forty minutes later, damages to the building estimated at approximately $500,000 had been caused. The only injuries to personnel were minor ones in connection with fire fighting.

Pertinent Facts: The end (north) section of the three-story building is of unprotected steel and steel grating floor construction. (See sketch) The adjacent section is unprotected steel with concrete floor at second level and open steel grating at the third level. The wall between these sections is concrete block to the second floor and corrugated transite from the second floor to the roof. The roof is concrete slab and two sides of the enclosed section are also corrugated transite. A concrete block wall from ground level to roof on the south side of the enclosed area separates it from other sections of the building. This wall and the concrete block wall enclosing the electrical and instrument control room at ground level were quite effective in preventing the spread of fire from the area of origin.



A 250 gallon cylindrical vessel, indicated on sketch as "wash tank", is used to recover valuable process components from spent filter sections. Solvent is fed into and through the vessel from a two-inch supply line at approximately 50 psig. The vessel is emptied through two valved sections connected to a drain line leading to another area, with appropriate valves at that point which are kept closed when the line is not being used. It was also equipped with a rupture disc with vent line extended outside the building, steam and nitrogen purge lines, and other necessary gauges, connections, etc.

The wash tank had not been used for a week prior to the fire, and the removable top section was in place, but unbolted, which was normal practice. The solvent supply line, which entered the building approximately ten feet from the wash tank, was equipped with a valve near the wash tank, and was under pressure because it also supplied the solvent for a similar use in another section of the building (not involved in the fire).

On the day of the fire, extension handles had been installed on the two valves in the two pipe sections connected to the drain line leading from the wash tank. These valves were then operable from the third floor near the solvent supply valve. This work was completed about 1-1/2 hours prior to the start of the fire.

Burning and welding was in progress at the third floor level of the open north section of the building, and turning was also done at the ground level. Sparks from the third level fell through one, and sometimes two levels of floor grating which probably helped scatter them. At the ground level wetted tarpaulins covered a drainage trench and equipment in the area and a safety man was hosing down the extensive area in which sparks were falling. The construction man at the ground level completed the burn-off of a pipe and stepped back to observe the safety man hosing the area. About this time he detected a strong odor of the solvent, and looking up saw liquid running down the north masonry wall of the control room, covering an area about twelve feet wide and already spread over a small area at grade level. He started to shout a warning to the welder on the upper level to stop welding when the vapors ignited near or at grade level and the flames quickly followed the liquid up the building wall. The fire was immediately observed by others in the area, the fire alarm was turned in and several employees obtained dry chemical fire extinguishers and started discharging them onto the fire which traveled up the wall to the second floor level and then into the second and third floor levels of the transite enclosed sections. It was thought that the fire was being brought under control by 150 pound dry chemical units on the upper levels (the flames at ground level and on the outside masonry wall had been extinguished) when a sudden jet of flame shot out from the general area of the wash tank and forced retreat of the fire fighters.

One hose line was quickly put into operation by area men, and the plant fire brigade arrived a few minutes after the alarm sounded and put three more lines in service. Fire fighting was difficult because of the intensity of the fire and inability to reach burning areas with the fire streams, particularly during the early stages when the corrugated siding was intact. The city fire department was called in and with their assistance the fire was brought under control approximately forty minutes after it started, and completely extinguished twenty minutes later.

Subsequent investigation resulted in the following well-established conclusions:

1. The valve on the solvent feed line to the wash tank was open about 1/4 turn. The flow through the partially opened valve was adequate to fill the wash tank in one to two hours.

2. Solvent flowed into the wash tank and, due to the valves in the drain line being closed, overflowed around the loose top, down onto the second floor concrete, across the floor to a door opening in the north side, and down the outside of the concrete block wall of the control room to grade level, where it was ignited by cutting or welding sparks.

3. The heat melted one or more sections of the aluminum line which contained solvent under pressure. This added considerable fuel to the fire and forced fire fighters from the area. The pump was shut down, however, approximately five minutes after the fire started, due to electrical cable failure. A total of approximately 350 gallons of solvent was consumed in the fire, indicating about 100 gallons had spilled from the wash tank overflow and the melted supply line.

4. The intense heat from the solvent fire melted other aluminum lines including those containing other organic solutions with a relatively high flash point. As a result, 1500 to 3000 gallons of organic liquids were drained from the vessels and consumed, increasing the fire intensity and subsequent building and equipment damage.

Preventive <u>Measures:</u> Provide a power cutoff button at the process control panel and at building exit to shut off all hazardous power to the operating area. Consideration should be given to maintaining power on the water pumps and possibly other units if this is feasible. Survey other plant areas to evaluate the need for similar master shutdown buttons.

Provide solvent pump shutdown switch in process control room.

Before solvent is used at wash tank again the following changes should be made:

1. Blank solvent supply line when not in use.

2. Install a catch pan under the wash tank which will drain to a collection tank.

3. Provide a 150 pound dry powder fire extinguisher on the filter floor with permanently installed nozzles directed at the wash tank and a remote operated valve in the field.

It is also recommended that a review of the wash tank operating procedure be undertaken with the objective of obtaining closer surveillance during times when it is being used.

Evaluate other gaskets for solvent service.

As an alternate to third paragraph this section (Preventive Measures), use a high flash point solvent in the wash tank instead of the more flammable one now in use. (This requires technical evaluation.)

Dry powder fire extinguishers should be on hand any time any other equipment which has contained solvent is opened.

Blanks should be used in solvent feed lines to other pieces of equipment in which solvent is used intermittently.

Where blanks are to be used in lines, block valves ahead of the blanks should have "Teflon" discs instead of metal to metal sealing surfaces.

Evaluate means for complete removal of highly flammable solvents from the plant.

Burning and cutting procedures should be established which will insure confinement of sparks to the greatest practical extent in areas where flammable solvents are used or combustible materials are present.

Review plant firefighting facilities and procedures in the light of this fire to evaluate again such items as number of hose boxes, desirability of stand-pipes in process buildings, and water supply and pressure. The investigating committee has not concluded existing facilities are inadequate but in view of the demonstrated potential for a large fire they should be scrutinized carefully.

CASE HISTORY NO. 634

Tank Repair Explosion

Description: Shortly after 12:00 noon, two leadburners entered a tank to continue repair of the lead lining. Another remained on top at the manhole to serve as watcher. One passed over the general area of the crack in the lining with his torch while the other prepared the lead rod to be used. The first spotted the flame about one inch above the crack and proceeded to burn through the lead. At approximately 12:30 p.m., when the torch had burned through, a minor explosion occurred, blowing out the flame. Both climbed down their ladders to the bottom of the tank, shifted one ladder to the manhole and climbed out of the tank. The explosion was great enough to blow the cap off the head of the leadburner serving as watcher outside the tank, and to cause the lead lining to vibrate against the tank wall. No one saw any flash and no surfaces were hot after the explosion. The only damages noted were (1) an enlargement of the hole where the leadburner had burned with his torch, (2) the lining was separated from many of the studs which fasten it to the tank wall, and, (3) a bulge in the lining, which had previously been hammered into place, had reappeared.

Leakage from this tank was first noticed during the split shift about two months previously. Material was leaking on the outside surface of the tank from one of the studs supporting the lining and located about six feet above the ground. Arrangements were made to temporarily stop the leak externally with a cement. The department continued to use material from this tank until no more could be transferred. Operations were then switched to a second storage tank.

Further cleanout of the tank was delayed pending a change in wind direction to avoid damaging spray-out during quenching. Finally ten days prior to the explosion at about 2:00 p.m. the department supervisor and foreman arranged for quenching the tank with water. The amount of fumes evolved was negligible. Cleanout was continued with three water and three lye washes followed by three additional water washes. Each wash was retained in the tank for about 24 hours.

The day prior to the explosion, after final water washing, a check for explosive vapor mixtures gave negative results. On the day of the explosion, the vapor test was repeated and a lighted torch was lowered into the tank to further test for flammable gases. Following this, the two leadburners entered the tank to make the necessary repairs. All normal precautions, such as completing fire and tank entry permits, blanking of lines, use of air mover, wearing of harnesses and eye protection, were taken.

The lead lining was in remarkably good condition after approximately ten years of service. The only defects noted were the crack which was the source of the leakage and bulges in the upper third believed to have been caused by vacuum created when the tank vent was blocked and material was being pumped to the department.

Externally, the painted tank surface appeared to have been damaged by leakage around some of the nuts to which the lining studs were secured and by internal corrosion resulting in barnacles erupting through the paint.

The tank has a 3/4-inch nipple on the bottom to allow any material trapped between the tank wall and the lining to drain. This nipple had been inadvertently covered with insulation; however, the insulation was removed and a rod was inserted through the drain to clear it and to puncture the lining before the tank was drained and washed.

Normally the leadburners remove all bulges in a tank lining before they perform any repairs requiring a torch. In this case they were instructed to repair the crack until arrangements could be made to have carpenters erect scaffolding from which the bulges could be reached. Following the explosion, one leadburner re-entered the tank and with chisel and hammer cut into one of the bulges. Fumes which evolved from the cut were so irritating that no work could be performed in the tank without a gas mask.

Cause: From the evidence available, the Committee concluded the following:

1. Normal precaution was taken and all existing procedures were followed in preparing and entering the tank.

2. Probably $POCl_3$, which passed through the crack in the lining, was trapped between the tank wall and the lining resulting in the fumes when the bulge was cut and in the leakage and barnacles noted on the outside surfaces.

3. Ignition of an explosive gas must have occurred to result in enough force to move the lead lining and to blow the watcher's cap.

4. The gas could possibly have been hydrogen generated by the action of $POCl_3$ and moisture on steel. The hydrogen generated could have collected in the bulges in the lining.

Preventive Measures: Develop design standards for providing drains and vents on lined vessels to prevent accumulation of liquid or gas between the lining and the wall of the vessel. Design should include positive means to assure that vents will not be covered with insulation.

Instruct the appropriate mechanical groups to vent all pockets in lined vessels where flammable gas can accumulate before using spark-producing tools or lighting a torch. A vapor test should be made after the gas has been vented.

Redesign the $POCl_3$ venting system to prevent future collapse of the linings, to insure against atmospheric pollution, and to improve housekeeping.

CASE HISTORY NO. 635

Implosion and Fire

Description: Two chemists were engaged in an experiment involving the recovery of a high melting organic compound from a methyl alcohol and glycol solution. They were using a 22-liter flask located under a large, open-front hood in a chemical laboratory.

Atmospheric distillation had been completed and some vacuum was applied to remove more of the methanol from the slurry. Shortly after the limited vacuum was applied, the flask imploded, throwing its contents over the man standing in front of the flask and to a lesser extent over a man kneeling on the floor and almost completely missing a third man.

The material flashed into flame, probably ignited by the electric heating mantle used to heat the flask. The two men, already on fire, ran away from the fire, but one man tripped over a flask of methyl alcohol on a scale in an aisle normally unused by the operating personnel. This methyl alcohol soaked his feet and pants legs and immediately ignited. By this time both men reversed direction and returned to a safety shower which was next to the hood. The safety was too close to the hood and fire to be usable. The most seriously injured man was pushed out an exit door by the second man. The second and third men, looking for water, tried to beat out the flames. They went to the men's room across the hall to finish extinguishing the fires in their clothing with water from the sinks. Most of the sprinklers went into action after the men left the room.

Cause: The exact cause of the flask failure is not known, but it is possible that distillation had proceeded to a point which allowed dry material to cake against the glass surface and create a hot spot. Operating temperature was about 140 degrees C.

Preventive Measures: This incident indicates the importance of the following points:

1. Safety showers should be outside of exit doors.

2. Aisles in laboratories should not be blocked, especially by hazardous materials.

3. When flasks are under vacuum, an upper mantle will retain much of the material.

4. Shields may be used to advantage.

5. Materials which form a suspension or slurry should be stirred to prevent formation of a crust on the sides of the flask.

6. Whenever possible, fixed, metal kettles or reactors designed for vacuum service should be used.

CASE HISTORY NO. 636

Men Exposed to Hydrocarbon Fumes-- *Fatal Fall From Tower*

Description: A canvas shelter had been erected on the top platform of a hydrocarbon purification tower. This weather shelter enclosed the top platform and it was heated with a steam heater. In the course of cleaning and inspecting the inside of the tower (the men entered the tower from the top) a sudden surge of liquid hydrocarbons was ejected into the shelter from a vent. The men, choking from the fumes, immediately tried to escape by way of the fixed caged ladder. One man, evidently overcome with the fumes, fell down the caged ladder to the nearest landing (approximately 40 feet). He died immediately from multiple skull fractures and a broken neck.

Cause:

1. A vent line from an adjacent blow-down tank ran up the side of the tower and exhausted about seven feet above the tower platform. This vent exhaust was covered by the canvas shelter.

2. A "low spot" in the vent line permitted the condensed hydrocarbons to accumulate

and eventually surge out of the vent exhaust after pressure build up.

3. The operating personnel failed to recognize the vent hazard and assumed it vented into the atmosphere above the shelter. (A visual inspection by operating personnel was not made before the job was started.)

4. The maintenance personnel had assumed the vent was inactive since the tower was not in operation.

Preventive Measures:
1. A section of the vent line was removed to eliminate the "low spot" and to promote drainage back into the tank.

2. An alternate vent will be tied into the main vent to by-pass the tower when necessary.

3. Improve communication between operating and maintenance personnel by conducting a joint briefing and safety meeting before the job is started.

4. Investigate Chemical cleaning methods to keep tower entry to a minimum.

CASE HISTORY NO. 637

Fume Exposure Aggravates "Nervous Stomach"

Description: Hydrochloric, chlorine, and chromyl chloride fumes are discharged to an outside ground-level pit where they are absorbed in weak refiltering solution of soda ash and periodically discharged through 8 inch tile overflow into a sewer line. The sewer line had caved in about 20 feet from the pit and was to be replaced and relocated. While employee was breaking old concrete with an air hammer in 3 to 4 feet deep trench about 10 feet from the neutralizing pit, he smelled some fumes which apparently had seeped through the pit overflow into the ditch. He climbed out of the ditch on two successive occasions before experiencing shortness of breath and nausea--and reported for medical attention. Although he responded favorably to administration of oxygen at plant dispensary, he was hospitalized for observation and treatment when nausea reoccurred. The employee has a history of general intestinal disturbances over the past several years. It is believed that anxiety concerning his slight fume exposure aggravated this personal condition.

Cause: Possibility of escaping fumes in this area had not been recognized by supervision.

Preventive Measures: Further work on the sewer will be done with the manufacturing unit shut down and tank-entry procedure will be applied to all similar jobs in the future.

CASE HISTORY NO. 638

Dehydration Press Explosion and Fire

Description: Difficulties had been experienced with the vacuum system of a nitrocellulose dehydration press less than an hour before an explosion in the press. The vacuum system did not pick up alcohol to be pumped through the compressed nitrocellulose and high pressure could not be established on the press. However, two blocks were finally processed and the press recharged. Again, difficulties were experienced. Fire and explosion occurred while the top ram was under higher pressure. Investigation ruled out the following possible causes: Friction created by foreign body or rapidly-descended ram, unstable nitrocellulose, and impact of dry nitrocellulose.

Cause: Believed to be adiabatic compression of a pocket of an alcohol vapor-air mixture or other gas.

Preventive Measures: When any abnormal or out-of-sequence operation of the press is noted or required, the cycle will be stopped, the upper ram brought to the top resting position and the nitrocellulose block ejected. If for any reason this cannot be accomplished, supervision will be contacted for remedial action.

CASE HISTORY NO. 639

Operator Forgot to Use the Emergency Shower

Description: A chemical operator at work during the third shift, needed to make some chemical adjustments to process liquor by addition of a relatively small quantity of Acid Sulfuric 93%. The tank in question was a 2,000-gallon process vessel. The tank opening could be reached by ascending a flight of stairs to the tank platform.

The operator poured a quantity of Acid Sulfuric from a carboy located on the floor into a stainless steel pitcher, then started up the steps to the tank platform. He stumbled, struck the pitcher against the steps and acid was splashed on his neck, arms and shoulder.

A fellow employee working at the opposite end of the floor, was using a water hose to clean a filter press. Seeing his fellow worker coming to him with acid on his clothing, he attempted first to wash off the acid. Then he cut off his clothes and continued to flush off his body. At the time this was going on, both men were standing almost directly under a very effective emergency shower but did not use it. Burns received at the time of this accident were hard to heal and almost three months later, it became necessary to resort to skin grafting for correction of the injury.

Cause: When Sulfuric Acid is spilled on cotton clothing, the clothing begins almost immediately to char and to lose its normal porosity. When acid-saturated cloth is then hit with an insufficient quantity of water, the acid-saturated cloth heats up very rapidly and can aggravate the chemical burn by heat.

The emergency shower would have provided much more water than the hose and permitted removal of the clothing while continuing to flush the body.

Preventive Measures:

1. The carboy of acid will be kept on the tank platform so that operator will not need to carry acid in an open pitcher up the steps.

2. Operators in all areas who handle corrosive liquid chemicals should make sure that they know where the nearest emergency shower is located in their area.

3. In the event anyone should be splashed with a corrosive liquid, remove affected clothing while operating the emergency shower.

CASE HISTORY NO. 640

Operator Failed to Follow Standard Procedure

Description: A chemical operator had completed the first half of a vacuum distillation of an organic acid (melting point of 133°C.). As this material is distilled under vacuum, the distillate must be received in a pan enclosed in a vacuum receiver. A relatively small quantity of sublimate normally coats the inside of this receiver as well as the receiver door. Because of this sublimate which occurs normally, but also because of the possibility that under abnormal operating conditions very hot and molten distillate can collect outside the receiver pan, standard operating procedure requires that a second pan be placed on the floor and under the receiver door before it is opened so as to catch any spilled material.

On this particular occasion, the operator did not have this pan in place under the receiver door before starting to remove the distillate from the receiver pan. Also on this occasion, distillate had collected in a molten pool inside the receiver and outside the receiver pan. When the crust was disturbed, the hot liquid ran out and some ran down his leg and into his open shoe, burning his foot.

Cause: Because the possibility that molten material can be present outside the receiver-pan and inside the receiver was anticipated, adherence to standard procedure would have provided the necessary protection from injury. Standard procedure was not, however, followed and the injury resulted.

Preventive Measures: Operators responsible for the operation of this equipment have been instructed concerning danger that can result from unauthorized modification of standard procedures.

CASE HISTORY NO. 641

Error in Opening Line

Description: A laboratory employee loosened a plug in a "T" of what he thought was a solvent feed line. Observing the material begin to "smoke", he realized he had mistakenly loosened a "T" plug in a catalyst mix line (aluminum alkyls and solvent). Attempting to retighten the plug, he turned it the wrong way and it fell out of the "T". Catalyst mix flowed out on the floor approximately three minutes before it ignited. During this time, four operating employees attempted to depressurize the line to stop the flow. One of the operators received moderate burns to his face.

The catalyst mix line mistakenly opened actually was a fill line leading to a dip pipe in a storage vessel. Ten pounds of inert gas on this vessel forced material out through the dip pipe and the open "T". Once started, the material continued to siphon in spite of release of the inert gas pressure. The flow of material and fire was stopped by a plastic plug being levered into the open "T".

Cause: The laboratory employee failed to consult with operating personnel for positive identification of line and proper procedures for opening the line for sampling.

Design of the process lines did not include check valves, or shutoff valves, to permit closing of the catalyst mix line to stop the flow caused by pressure or siphoning in the event of accidental opening or breaking of the line.

After the leak occurred, four operating employees performing emergency procedures to stop the flow, exposed themselves to material and vapor that possessed self-ignition properties.

Preventive Measures: Check valves have been installed on the fill lines to catalyst mix tanks.

Shut-off valves have been installed in fill lines.

Before any line is opened in the catalyst mix area, a hot sheet must be obtained from the shift supervisor. This includes sample taking.

Opening of equipment in the catalyst area will be done by operating personnel only. Two men will be in the area while this work is done.

Personal protective equipment will be placed in strategic locations.

CASE HISTORY NO. 642

Foreman and Chief Operator Sprayed by Chlorosulfonic Acid

Description: A foreman and the Chief Operator were sprayed with chlorosulfonic acid (CS). The Chief Operator was pouring an 8 oz. bottle of CS sampled from an acid truck into the process sample drain line. Chlorosulfonic acid "blew back" spraying both men. The drain line allows CS to flow by gravity into a catch tank for reworking.

The foreman had been checking the CS process and decided to collect a grab sample directly from the finished product line. He opened the 1/4-inch sample valve and started flushing out the line. Chlorosulfonic acid was draining into a glass funnel, through a 1-inch pipe line into a 300 gallon catch tank. At this time, the chief operator approached and showed him a CS truck sample. The chief operator started pouring the sample into the funnel. He had poured out less than half of the sample when he was sprayed in the face, neck, chest, and right knee with CS. The foreman, standing behind him, was sprayed in the face, shoulders and both arms.

They immediately jumped back and stepped under a nearby safety shower. A maintenance foreman, sitting in his truck in front of the machine shop, saw the white cloud given off when the CS "blew back". He radioed the dispatcher to alert the safety office. He then drove the injured men to the dispensary.

Cause: The causes of the accident were poor design and improper procedure.

1. The CS drain line had a low point between the funnel and the catch tank where water probably collected.

2. Neither man was wearing the proper eye and face protection required when sampling a process stream. Both men were wearing safety glasses only.

Discussion: The sample point and drain line in the CS process is used infrequently. It was last used about a week before for a series of samples.

However, an open glass funnel remained in the drain line whereby, rain or water from another source could easily have gotten into the funnel and drained to the low point in the 8 ft. long pipe line.

It is the opinion of the Investigation Committee that water or weak acid had collected in this pipe line. After the foreman had started flushing out the CS sample line and as the chief operator was pouring the truck sample into the funnel, CS came in contact with the collected water. The violent reaction of CS and water caused acid to "blow back" through the pipe, out the funnel and spray both men.

It is believed that the safety glasses the chief operator was wearing prevented a serious eye injury and possibly saved him from losing the sight of his left eye. However, neither man was wearing the required eye protection when sampling a process stream. If they had been wearing goggles and a face shield, their heads and faces would not have been burned.

Also, there was not sufficient water available from the safety shower. Possibly the severity of their burns would have been reduced if more water were available.

Preventive Measures:

1. Instruct department personnel that goggles and face shield are required when sampling a process stream.

2. Replace and relocate the existing sample point with one that is in a less cramped position. Also, insure that the drain line has no low points for pockets of CS or water to collect. Install a cover over the funnel to prevent rain or other foreign material from entering. It was recommended enclosing all four sides instead of three sides.

3. Make sure the safety shower has the required amount of water.

CASE HISTORY NO. 643

Flash Fire in Exhaust Duct

Description: A flash fire occurred on the roof of a building at 12:25 P.M. It was followed within 30 seconds by a second flash fire at the mouth of the kettle containing Vinyl Butyral solution. Both fires were put out quickly with fire extinguishers and there was no personal injury or equipment damage. The investigation of the incident indicates that the fire started at the exhaust of the Vinyl Butyral vent pipe as a result of foreign material in the fan or static. The fire then flashed back down the vent stack to the kettle. Quick, efficient action by the operating personnel resulted in putting the fire out without the assistance of the city fire department, which responded to the alarm.

Conclusions: The fire started on the roof of the building in the immediate vicinity of the exhaust fan. When the exhaust fan was shut off or by-passed by the burning of the rubber connecting hose between the vent pipe and the fan, the flame flashed back down the vent pipe into the kettle. This resulted in the second fire.

The initial fire started when a spark occurred in the exhaust system which was conveying a flammable mixture of alcohol fumes. This spark was either the result of a foreign body in the fan or static from flow through the pipe.

A number of exceptions to the Class 1, Group D electrical requirement of this building were noted during the investigation. None of these were directly involved in the accident but they do show the need for increased emphasis on maintaining high safety standards in this building.

Preventive Measures:

1. Review and revise Vinyl Butyral process and equipment to insure no safety factors have been overlooked. Do not produce any more Vinyl Butyral resin until this is completed.

2. Inspect building for conformance to Class I, Group D electrical standards and correct as necessary.

3. Re-emphasize safety requirements of building to all operating and maintenance personnel through meetings and signs.

CASE HISTORY NO. 644

Acid Sprayed from Tank Truck Hose

Description: The injured, a truck driver, was making a delivery of 66° Sulfuric Acid to the customer's plant. He was alone. Connection is made from truck to tank by a rubber hose having four bolt flanges on either end. The receiving pipe runs parallel to and only five inches away from a fence. This makes it awkward and difficult to work two of the bolts. Accordingly, only two are used and have been for years. The bolt nearest the fence was first made tight, then the opposite one. Valves were opened, the truck air compressor started and 12 psig put on the truck tank. The driver walked to the rear to make sure all was well. His knee struck the hose. The bolt near the fence popped out and a large stream of acid struck him even though he was five feet away. He secured the air and compressor to stop the flow since he was only five feet away from a public road over which he knew school children were soon due to pass. He ran into the customer's building, calling for and getting help and water (about 150 ft. away). His Acrichino coveralls were covered with acid but, when removed, the clothing underneath was not burned. Serious eye injury was undoubtedly avoided because he was wearing goggles. He was taken to the local hospital for treatment and released.

There was evidence the flange bolts were old and partly corroded.

Preventive Measures:

1. Service group to review existing rule that all flange bolts must be secured. Truck drivers shall not pump unless all bolts are properly in place.

2. Drivers to maintain supply of new bolts and nuts in truck for use if existing ones show evidence of corrosion or wear.

3. Service personnel to report inadequate facilities or congested, dangerous areas to our Safety Department, also the Sales Department. The latter should make every effort to get the cooperation of the customer to remedy situations dangerous to our personnel. Our safety program does not stop at the plant boundaries.

CASE HISTORY NO. 645

Centrifugal Machine Went Wild

Description: At approximately 3:30 A.M., the loaded basket of a 48-inch suspended type centrifuge became unbalanced and started a chain reaction noted below:

1. The plow blade became imbedded in the product cake in the basket.

2. The plow blade was broken away from its shaft.

3. The lateral movement of the plow shaft broke its supporting cast iron bracket, operating wheel and counterweight cable and exerted sufficient force to shear off four 3/4-inch diameter bolts fastening the casing to its base plate.

4. The counterweight cable wrapped around the basket shaft.

5. The plow shaft fell into the basket and sheared off the feed pipe spray nozzles and bent the 1 1/2-inch feed pipe.

6. The shaft flew out of the basket and struck and broke a nearby 6-inch cast iron tee on the outlet nozzle of an adjacent centrifuge.

Discussion: At the time of this incident, the centrifuge was being operated by an operator with some eight years' experience. His reactions during this period were commendable as noted below in his version of what actually took place.

1. About 2:00 A.M., the centrifugal motor began kicking out during a loading operation. An electrician was called, could find nothing wrong and the trouble was attributed to an overload in the basket.

2. Following instructions from the premium operator, he cleaned the machine but did not notice anything that would indicate the existence of a hole in the basket cloth. The only unusual thing noticed was that a slightly thicker than normal layer of cake remained on the bottom of the basket.

3. He then started loading the machine and, although experiencing some difficulty, had just about completed the loading when the basket began gyrating so wildly that it scraped against the casing causing sparks to fly out. He immediately hit the stop switch, turned off the valve in the feed line and attempted to apply the brake.

4. When the brake was wrenched out of his hand, he dashed some thirty feet away from the machine to where the premium operator was working. It was just about this time that the plow assembly broke apart.

5. When things stopped flying around, he returned to the centrifuge and used the brake to stop the rotating basket.

It is the opinion of this Committee that this accident was caused by the sudden shift of the center of gravity of the load in the centrifugal basket resulting from the sudden escape of an appreciable amount of cake from one side of the basket through a hole in the basket cloth.

It is very probable that the operator would have been injured had he remained in front of the centrifugal as a broken piece of the plow handwheel was found in back of his normal working position.

The Committee believes that provision should be made to enable operators to stop the slurry feed pumps from the platform immediately above the pumps in cases of emergency, i.e., a flying object breaking the slurry pipe upstream from feed valves at centrifugals.

Preventive Measures:

1. Have operators clean centrifugal and check condition of basket cloth each morning.

2. Have operators check automatic motor cut-off switch on break handle each morning to see that it is working properly.

3. Provide additional stop stations for the three slurry feed pumps on handrail of platform where premium operator normally works.

General:

1. Spray nozzles to clear maximum thickness of cake by at least one inch.

2. Plow counterweights on all centrifugals to be made sufficiently heavy to retain plow in up position when it is not being used.

3. Request Plant Technical Service (PTS) to design a positive locking device that will prevent plow from rotating or moving downward when not being used.

4. Request PTS to investigate feasibility of installing a device, similar to those installed on existing centrifugals in Department 262 which will automatically shut off the centrifugal motor and brake the basket whenever shaft deflection becomes excessive.

5. Maintenance Department to set up routine centrifugal tear-down inspection program.

6. Maintenance Department to post centrifugal inspection reports.

CASE HISTORY NO. 646

Sodium Peroxide Burns

Description: Two operators were unplugging a four-inch diameter dust drain line in a collection system. To dislodge built-up sodium peroxide, they had opened several one-inch clean-out ports to insert rods and had used sledge hammers to pound on side of equipment and piping. The chief operator was rodding a port while the other operator was hammering on collection hopper at top of equipment when a dust cloud issued from the port, striking the chief operator on his face and arms. His goggles undoubtedly saved his eyes; his arms were burned through his shirt sleeves.

Cause: Equipment design permitted dust hold-up.

Preventive Measures: Equipment is being redesigned to eliminate dust hold-up and necessity for rodding. If clean-out is required before change over to redesigned equipment, face hoods will be worn by employees doing this operation.

CASE HISTORY NO. 647

Safety Overlooked in Set-up of Experimental Equipment

Description: A plug-up had occurred in line leading from continuous-nitrator slurry pump into boiling-tub house in pilot-plant set-up. While the pump was being unplugged, the nitrator vessels (containing mixed nitric and sulfuric acids) began to heat spontaneously and were cooled to normal temperatures with water from a hose. When operators decided to "ditch" or drop the charge into the plant filters, their helper was directed to stand at switch for under-flow agitator between two nitrator vessels and to start the agitator at a given signal. When he turned the switch "on", acid immediately sprayed on him from inspection door at top of one vessel. He left the immediate area toward exit of building, returned through spraying acid to stop the agitator, and then left the building out the safety chute. He sustained burns on one eye, his face, neck, back and lower part of one leg.

Cause: Poor layout or arrangement of this experimental equipment.

Preventive Measures: The agitator switches have been moved outside the building. The agitator has been slowed from 1750 RPM to 435 RPM, the safety shower has been moved to a more accessible location, and operators will wear Neoprene protective clothing when starting up, shutting down, and during emergency conditions.

CASE HISTORY NO. 648

Hydrogen Cyanide Exposure

Description: An employee was performing an operation whereby sodium cyanide was used as one of the basic ingredients for a chemical reaction. Adequate ventilation was provided for this reaction.

During the operation the heat of the reaction was sufficient to cause the methyl alcohol solution which was saturated with hydrogen cyanide and product to boil over and spill onto the floor. During this reaction, hydrogen cyanide gas is present; this gas is both toxic and flammable. When the spill occurred, the operator, who was assisted by a fellow employee, backed away from the reactor, picked up available water hose lines, and proceeded to wash down the floor. The fellow employee was located in an area to the east of the kettle and the operator was located approximately 25 feet west of the kettle. During the cleaning up operation, apparently hydrogen cyanide gas was given off in sufficient quantity whereby the operator was overcome and he fell to the cement floor, striking his head on the right side.

Other fellow employees in the area saw him fall and immediately went to his aid. They sounded the emergency alarm which served to tell all the building occupants to get out of the building. The injured was removed from the building and first aid was administered by fellow employees by the use of amyl nitrite pearls, broken and held lightly over his nose. The Medical Department was summoned. Additional first aid consisted of supplying oxygen from an inhalator and the injured employee was covered with a blanket to keep him warm.

The injured employee was treated at the Medical Department and permitted to return to his job on the following day. Certainly the first aid which was given to the injured employee should be highly commended; however, it is well to point out some of the hazards involved when working with cyanides. They are poisonous by:

(a) Ingestion
(b) Dust inhalation
(c) Absorption through the skin
(d) In contact with acids they liberate hydrogen cyanide gas which is both toxic and flammable.

Emergency Measures: If hydrogen cyanide gas is released during a reaction to endanger people, the following emergency measures should be followed:

1. Sound the alarm and have all personnel removed from the area.

2. Avoid any cleaning up operations until the personnel have been provided with proper respiratory equipment.

3. Workers who may be exposed to sodium cyanide should be provided with:

   a. Cotton gloves when handling solid sodium cyanide.

   b. Rubber gloves for handling sodium cyanide solutions or articles coming from cyanide baths.

   c. Safety goggles or full face masks when operating molten cyanide baths.

   d. Asbestos gloves should be available at all times when molten baths are operated.

   e. Proper respiratory equipment, if there is a possibility of exposure to sodium cyanide dust or to hydrogen cyanide gas.

   f. Adequate instructions for frequent washing of exposed parts of the body; namely, face and hands.

g. Safety showers, eye baths, and first aid equipment.

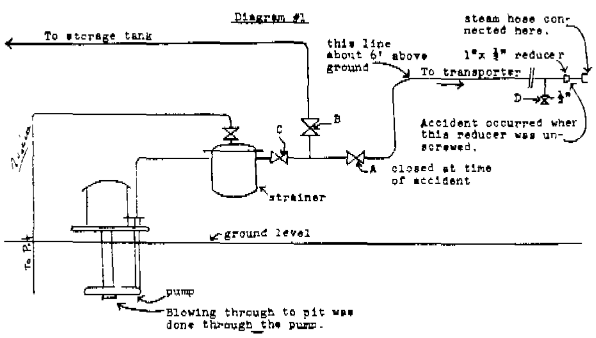
The above incident sets forth the need for adequate operating procedures which must be followed at all times. Such procedures should be reviewed with operating personnel at frequent intervals to make certain that all necessary precautions are understood. The first aid which was administered by fellow employees at the time of this incident was instrumental in minimizing effects of cyanide poisoning to the injured employee.

CASE HISTORY NO. 649

Molten Sulfur Sprayed on Face and Chest

Description: There was difficulty pumping molten sulfur from the sulfur pits to the storage tank on the west side of Building 60. The strainer on the discharge on the pump appeared to be plugged and the line from the jacket of the strainer to the trap was removed to allow steam to blow free through the jacket to melt out the plug.

A steam hose was then run from inside Building 60 about 50 feet and attached to the flange at the end of the unitrace line, which is used to load the sulfur transporter (see attached diagram #1).



The steam was turned on and the line was blown through to the storage tank, through Valves A and B on the diagram. Valve B was closed and Valve C opened to blow through to the sulfur pit. This was continued until a froth began to build up on the sulfur, at which time the steam valve in Building 60 was closed and when the pressure was bled off, Valve A was closed. Valve D was then cautiously opened to check for pressure in the line, but it was apparently plugged.

A steam hose was disconnected from the coupling and found to be plugged with solid sulfur. A repairman then started to remove the steam hose connection at the reducer (see sketch on diagram). He proceeded very carefully, looking for signs of pressure, but there was apparently no pressure. When the reducer reached the last thread, it suddenly blew off, blowing molten sulfur out on the far side of the line from him, spraying another repairman and the department foreman.

Cause: Plugging of the hose and the unjacketed portions of the hose connection with sulfur.

Observations: 1. Leaving Valve A open might have prevented this accident.

2. The situation that led to this accident exists generally throughout the plant.

3. While the repairman removing the steam hose was not involved in the accident, he should have been wearing a hood in this instance.

Preventive Measures: The Committee recognized the situation which occurred here as being the same as every other instance in which a plugged line is steamed out. Every time we blow a line out with steam, we have, potentially, a repeat of this accident. The Committee considered design changes in the piping and in the hose connection to lessen the danger of this recurring in other spots. The Committee has only one recommendation:

1. Create more consciousness of this problem plantwide by publicity in departmental or plantwide safety meetings. Responsibility: All salaried personnel.

CASE HISTORY NO. 650

Phossy Water Burns on Face of Operator

Description: At approximately 7:30 a.m., two condenser operators were going to unplug a phossy water line by rodding. The line to the spray tower seal has a cap on top of a T where it enters the seal. The operators were unable to remove this cap and went to the next lower level and broke a union in the line. Returning to the upper level they inserted a 1/4-inch rod into the line, through the opening at the union. As the rod was pushed into the pipe, the obstruction was dislodged and hot phossy water sprayed into the face of one of the operators. The pump was off and steam had been applied to the outside of the line for some period of time before union was broken.

Cause: 1. Inexperience, new man (2 months).

2. Improper procedure.

3. Failure to use proper protective equipment.

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Preventive Measures: 1. Department supervision with the help of the Safety Department determine what protective equipment is needed and see that rule is followed.

2. Furnace foremen bring to the attention of all furnace plant people. All other foremen discuss in next regular safety meeting.

3. Continue on-the-job training with all new people.

CASE HISTORY NO. 651

Eye Burned by Spray of Hot Steam and Oil

Description: A fuel oil heat exchanger was allowing condensate to mix with oil indicating tube leakage. Upon visual inspection of the tubes, one tube was found to be plugged. A heavy wire ran through the tube until a light could be seen at the other end. The steam valve was then cracked to see if any steam was getting into the tube. When no indication of steam was found leaking into the tube, the injured employee bent over to look into the tube. Just as his eye was level with the tube, the obstruction broke loose from the tube allowing oil and steam to hit him directly in the left eye. He received severe thermal burns to the entire left eye.

Cause: Employee observing the interior of the tubes through the ends as steam was introduced. In addition, employee was not wearing required eye protection. It was indicated that sweat and steam on the eye protection did not allow a good view of the interior of the tubes, therefore, were not worn.

Preventive Measures: Better methods of tube inspection and other equipment are being developed. These will include no observation while steam is applied and strict adherence to established eye and face protection requirements.

CASE HISTORY NO. 652

Carbon Bisulfide Tank Car Accident

This "near miss" is being submitted because of the hazards and the volume of carbon bisulfide present. If during this accident a leak in the tank car had occurred, this could have been disastrous.

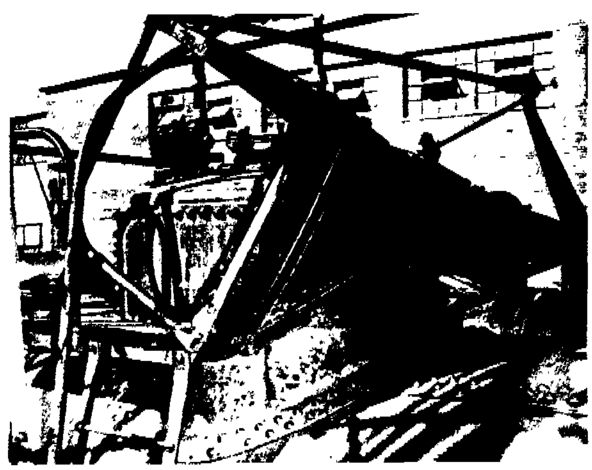
Description: A company switching crew was spotting some cars in a process area. As the train moved up the track, a free swinging loading pipe caught on the handrail on the top of one of the tank cars. The engineer was signaled to stop, but the damage was done before he could bring the train to a stop. One of the employees had to jump from the car to avoid being hit by the broken piece of loading pipe.

Cause: The process operators, who had last used the loading pipe, were questioned about normal disconnecting procedures. They stated that when the valve is disconnected, it is swung around to the back of the loading platform and lifted over the handrail. A flange on the loading pipe holds it securely to the handrail. Neither of the men could remember securing the loading pipe. Each man stated that he assumed the other operator had done it.

It is theorized that the unfastened loading pipe swung over the railroad tracks because of the vibration of the moving train.

Preventive Measures: 1. Each member of the unloading crew will have specific assignments for which he is responsible. This will insure that all phases of the operation are completed.

2. A more positive method of securing the loading pipe to the loading platform is recommended.



CASE HISTORY NO. 653

Sodium Meta Nitrobenzene Sulfonate Fire

Description: The double drum steam dryer in Department C-1 was being used to dry a 40 per cent water solution of sodium meta nitrobenzene sulfonate. The drying operation was being done under authority of "Addendum to Ethaven Process of 12-28-53" issued on March 17, 1960. The operation had started up on split shift of March 23.

Interrogation of the two operators in the department at the time the fire started revealed the following facts: The operators had shut off the auger in the bag packer; had ascended the stairs to the first level, and were standing by the dryer rolls to observe the drying rate. They heard a noise which they described as a small muffled explosion which apparently occurred in area of the leverpak receiving dry material. Immediately, the cotton skirt used to convey the dry material from the end of spout of the bag packer to the leverpak was observed to burst into flame. The flaming skirt evidently fell into the partially filled leverpak and ignited the dry material. One of the operators instantly called the plant fire department, while the other ran downstairs, grabbed a water hose and began playing water onto the fire in the leverpak and around the bag packer. A third operator entered the department and was given the hose. The operator then ran back up the stairs and cut off the feed solution to the dryer, reduced the steam pressure on the dryer rolls and shut off the splash feed mechanism in the dryer. The plant fire department arrived and extinguished the fire. Water and dry chemical were necessary to completely eliminate all fire which had spread through the bagging machine and into the hopper under the dryer rolls.

The dry product is known to have a fire point of 405-410°C in air and shows no sign of thermal decomposition at 300°C. However, contamination with oxidizable materials does lower the thermal stability. The Research Department re-ran tests on material which had been dried just prior to the fire to re-establish the thermal stability of the dry product. The original temperature of 300°C was found to be true again. In addition, thermal tests were run on the dry product in which 15 per cent by weight of cotton threads had been added and it was found that the stability had been reduced. (In the range of 127°-160°C heat evolution in the magnitude of .2 cal/min/kilogram is detectable.) The testimony of the eye witnesses indicates that a minor dust explosion occurred in the top of the partially filled leverpak. It is the consensus of the Committee that this ignited the material on the cotton sleeve and the flaming cotton sleeve ignited the product. The major portion of the damage was to the bag packer. The dust explosion is believed to have been triggered by a spark resulting from a built-up static charge since the bag packer was not grounded.

Conclusions and Immediate Action: From the investigation, the Committee has drawn the following conclusions:

1. The dust explosion was initiated by a spark resulting from a buildup of static charges resulting from the free fall of dry material over the non-conducting cotton apron.

2. The dust explosion ignited the dry material on the cotton cloth due to the fact that its thermal stability had been reduced by the presence of cotton.

3. The drying operation was resumed April 1 after completion of the following action:

   a. The bag packer was removed from the system and the product flowed directly into the leverpak from the hopper under the dryer.

   b. A well-grounded metallic skirt was installed to convey the dry material from the hopper to the leverpak.

   c. Two new sprinkler heads were installed under the dryer and directly over the leverpak being packed.

   d. Extra fire fighting equipment was placed in the department and all operators checked out on its use.

   e. Two men per shift were used on all shifts for the duration of the drying of this product. The men were instructed to never leave the department while the dryer was in operation.

   f. Filled leverpaks were removed from immediate area around dryer.

   g. Types of fire extinguishers were checked on an actual fire to determine best type to be used. (Water was found to be most effective. CO_2 and dry chemical were ineffective.)

CASE HISTORY NO. 654

Compressor Incident

Description: The North main air compressor was shut down on a crash basis at about 4:50 a.m. The machine was slow rolled with steam prior to uncoupling and at about 7:30 a.m. was uncoupled. The operator using a special wrench began the normal procedure of hand rolling a turbine. A chief operator and two supervisors were present. After turning the turbine shaft, the operator inserted the lugs on the wrench into the compressor half-coupling holes and turned the shaft a small amount in the direction opposite to normal rotation. Immediately, the compressor began rolling rapidly with the wrench hanging onto the coupling.

Personnel scattered from the area and the wrench came off like a projectile. Even so, it did only minor damage. Rotation of the compressor was stopped by blocking in the discharge valve tighter, and braking the shaft rotation with a board. This braking was necessary because leakage through the block valve and check valve was sufficient to roll the compressor.

Cause: The cause of this near-miss was the leakage through the discharge block valve and check valve rotating the compressor backwards. During a scheduled or non-crash shutdown of these machines, leakage through the block valve is probably less because the block valve can be closed more deliberately allowing better seating. The check valve was found to be badly corroded and could not seat. It is possible, though not confirmed, that air leakage could result in a wreck of this machine by overspeeding the machine in the reverse direction.

Preventive Measures:

1. A blind was installed in the discharge and various vents and covers opened to relieve any air.

2. The check valve and block valves will be overhauled on a routine basis during future unit shutdowns.

3. Maintenance procedures on these machines will include blinding both the main discharge and the discharge lines before actual work begins.

4. Engineering will reconsider the adequacy of this particular check valve design since it appears to be unsuited in this particular location.

CASE HISTORY NO. 655

Chlorine Line Ruptured from Excessive Pressure

Description: Employee was working on a chlorine barge, although no loading was in progress. One liquid chlorine line was still connected to a barge tank which was filled on the previous shift. Although the proper vent valves were open, it is believed that liquid chlorine became trapped in the loading line causing a flexible metal hose to rupture which in turn probably broke off the pipe line itself. The employee was in the immediate area and inhaled large quantities of chlorine gas resulting in massive pulmonary edema and lung hemorrhaging causing death. A pressure in excess of 1500 psig developed in the chlorine line which caused the chlorine flexible metal hose to burst. Valves were properly opened as attested by the loading foremen who closed the valves following the accident. It would appear that the bleed-off line from the liquid line to the gas line became plugged and permitted a pressure build-up in the liquid line. However inspection of all the lines involved did not reveal any signs of blockage.

Preventive Measures:

1. It has been made mandatory to evacuate and disconnect these chlorine lines to the barge whenever loading is interrupted for any reason.

2. The cross-over line from liquid line to the gas line has been enlarged to 1 1/2-inch size.

3. A heated expansion chamber has been provided in the liquid chlorine line.

4. A pressure alarm will be installed on the liquid chlorine line.

5. Operating instructions have been reviewed and discussed with each man. Operator will not be permitted to deviate from these written instructions without permission.

CASE HISTORY NO. 656

Crust of Solidified Alum Broke Allowing Employee's Foot and Leg to Enter Hot Alum Below the Crust

Description: The maintenance Foreman (injured) and the Alum Plant Foreman were standing on top of a pile of solidified Alum to inspect the underside of the mixer. The maintenance Foreman's right foot broke through the crust and his foot and leg entered the hot Alum to about 14 inches below the knee.

The evening before the accident 77% Sulfuric Acid and Bauxite were mixed. This was complete at 7:30 PM. The reaction heat is estimated at about 300 degrees F. This reaction causes hardening of the Alum in about 2 hours. The following morning the injured employee was inspecting the underside of the mixer for possible needed repairs when his foot broke through directly under the mixer spout into an area where solidification was not complete. Investigation 4 hours after the accident showed complete solidification of the alum. The pH of the Alum at this point is very slightly basic. The breakthrough point was almost exactly in the center of the bin, so it received the last of the mixture and less heat was carried away, possibly slowing the reaction time.

Preventive Measures: If it becomes necessary to inspect under the mixer or mixing floor again, it shall be done from a ladder when the bin is empty.

CASE HISTORY NO. 657

Acetylene Hose Rupture

Description: While employee was adjusting a pressure control valve on an acetylene cylinder, the hose ruptured near the valve.

The acetylene ignited and burned the employee. He received second and third degree burns on the left arm and the left side from the waist to the armpit. The acetylene hose was estimated to have been in service about five years. During this time, the hose had been flexed severely at the point of failure; i.e., where the hose connects to the pressure control valve. The flexing produced a weak spot in the hose that went unnoticed.

Preventive Measures: Periodic inspections and tests will be made of oxygen and acetylene hoses. These inspections will include immersing in water, hoses which are under normal working pressure. National Safety Council suggestions for safe use of hose in welding and cutting operations will be issued to all departments.

CASE HISTORY NO. 658

Explosion of Residue Inside Pipe

Description: A foreman attempted to cut a 1-1/2 inch Black Pipe line with an acetylene torch. The pipe had been used about 12 months ago for transferring nitrogen solution from tank cars to Mixer Weight Tank. The pipe line had been disconnected on each end some time ago and the employee was trying to dismantle the line by cutting it in sections with the acetylene torch. The residue in the pipe exploded with a terrific blast at the point of contact with the torch and the pipe was ripped open for a length of approximately five feet. Apparently some Nitrogen solution had been left in the pipe when it was last used in August, 1959, and a solid residue, presumably of ammonium nitrate, remained in the pipe. Heat from the torch caused decomposition and explosion of the material resulted. (Four men were injured - two disabling.)

The welder received the most extensive injuries consisting of deep lacerations and small bone fracture of left upper arm and forearm and fractures of third and fourth fingers on left hand. There is some possibility of loss of left forearm. His right ear drum was ruptured and the third finger on right hand was injured so badly that surgical amputation was necessary. He also sustained lacerations to stomach and legs. The second employee received a slight cut over the left eye and bruise on the left hip. The third employee sustained a slight concussion and a possible rupture of both ear drums. The fourth employee involved in this accident suffered a rupture of both ear drums which was accompanied by headache.

Preventive Measures: Strict orders in writing have been given to all operators of welding equipment, advising them that they must never use such equipment on pipe lines or vessels containing or being contaminated with Nitrogen Solution, Ammonia or other flammable materials.

CASE HISTORY NO. 659

Safety Disc Ruptures

Description: On March 16, 1960, at approximately 6:10 p.m., the safety disc ruptured on Research Pilot Plant Kettle #6 during a polymerization reaction. Upon rupture of the disc, flammable gas and vapors issued rapidly from the flange disc mounting and into the area immediately adjacent to the Kettle rather than out the safety vent line leading to the roof. Appropriate action to reduce the hazard was quickly taken by operating personnel and the building was evacuated. There were no personal injuries or equipment damage.

Pilot Plant kettles are normally equipped with two safety devices; a rupture disc and a pop valve, mounted in series. The rupture disc is the primary pressure relief device. Since these discs are subject to continual stress and frequently rupture well below their rated limit, the spring loaded pop valve is introduced into the vent line to prevent dumping a kettle full of dangerous vapors into the air adjacent to Research building. Under normal circumstances, the pop valve will relieve excessive pressure then reseat itself giving protection to the kettle while still avoiding the other hazard. The rupture disc here involved was rated at 170 - P.S.I. at 72°F, but it has been estimated that at the elevated temperature to which it was exposed it could have opened at 150 P.S.I.

In this particular instance, the rupture disc broke and the pop valve did not open. Instead the gases leaked out of the line connecting the rupture disc to the pop valve and filled the Pilot Plant area. Subsequent investigation disclosed that the pop valve which should have opened at 150 psi, would not open until the pressure exceeded 460 psi. It was also noted that a flange in the connecting pipe line had been drilled with three holes which were supposedly designed to eliminate a gradual pressure build-up between the rupture disc and pop valve so that the disc would not rupture at its designed limit.

Cause: The primary cause of the incident was, of course, the pressure rise within the kettle. The kettle had recently been equipped with a cascade temperature control system which had not been completely standardized.

Preventive Measures: 1. The temperature controller and procedure for its use shall be reviewed to guard against future pressure build-ups in the kettle.

Responsibility: Pilot Plant supervision.

CASE HISTORY NO. 660

Venting of Gas from Tank Truck Causes Explosion

Description: A truck transport had unloaded a trailer of acetaldehyde. Natural gas is used to pressure the tank in this operation. The transport was parked outside the plant fence to depressure prior to reloading with other chemical material.

During the venting, the mixture of acetaldehyde and fuel gas ignited from an unknown cause and ignited the tractor tires. The front compartment of the trailer ruptured due to internal explosion. The fire crew responded to the alarm and extinguished the fire within five minutes with water and dry powder. Water was used to keep the trailer and truck cooled to prevent re-ignition. All electrical equipment was disconnected.

Cause: The source of ignition was believed to be the tractor exhaust system. Although the engine was not running, enough heat could have been present to ignite the vent gases.

No injury to personnel resulted.

Preventive Measures: All personnel, including outside truck drivers will be cautioned to use extreme care when venting, to see that no source of ignition is present. Trailers will not be vented in near proximity to any plant installation or equipment.

It is planned that a vent stack will be installed a safe distance from the location where the truck is vented. A line will be connected from the vent on the truck to the vent stack.

CASE HISTORY NO. 661

Tank Truck Incident

Description: On February 8, 1960 at 12:00 noon, a three compartment tank truck (owned and operated by a contract hauler) containing vinyl acetate was delivered to the plant. The truck was backed into position at the unloading dock, the support legs were lowered, and the tractor was removed. The vinyl acetate was to be unloaded the following morning. At approximately 1:00 a.m., tne guard in making his rounds noticed that the right support leg of the truck had collapsed and had pierced the front compartment of the tank. The left front leg was deformed from the added strain, allowing the front end of the tank to settle down close to the ground so the valve box rested on the ground. The entire contents of the front compartment, estimated to be 2,500 gallons, spilled out into the yard resulting in a very hazardous condition. It was necessary to flush this area with fire hoses for eight hours in order to dilute and wash away the vinyl acetate. Fortunately, it was a cold night and the ground was frozen. Also, the area was pitched to the nearby river so the solvent could be flushed away.

Cause: An investigation showed that two of the bolts holding the support leg were missing. The fact that the tractor had been removed from the trailer without proper supports under the trailer was a contributing factor to this accident.

Preventive Measures: It was evident that the entire tank truck loading and unloading operations required close scrutiny and immediate change to prevent a recurrence. The following rules were incorporated into the tank truck loading and unloading procedure.

1. Tank trucks containing flammable solvents or corrosive material are never to be disconnected from the tractor. The wheels must be properly checked by the driver before unloading.
2. The tractors and tank trailers are to be removed from the plant as soon as they are empty.
3. No leaking or overflowing tank trucks are to be accepted.

CASE HISTORY NO. 662

Caro's Acid Suspected in Laboratory Explosion

Description: An explosion which occurred during the wet washing of a polymer sample was caused by the inadvertent addition of acetone to a solution thought to have contained Caro's acid, H_2SO_5.

The chemist received numerous lacerations and was hospitalized for four days. Three others received minor injuries. Glassware on the other side of the room was broken and a window eight feet away was cracked by glass fragments.

The work involved analyzing polymer for metals by modification of a procedure published in "Analytical Chemistry", February 1959. On the day prior to the accident, wet ashing of four weighed samples of polymer had been performed as follows: Approximately 0.8g of polymer sample was charred by heating with 20 ml of 95% sulfuric acid. Incremental additions of concentrated nitric acid and then H_2O_2 were made. The flask was heated on the hotplate until SO_3 fumes were evolved between additions.

On the following day, the four flasks were placed on the laboratory bench for the water dilution step. At this point, one or two ml of acetone were inadvertently sprayed from a plastic wash bottle into one of the flasks. At once the liquid started to effervesce and then exploded.

A literature search revealed that peroxymonosulfuric acid, Caro's acid, could be formed ($H_2O_2 + H_2SO_4 \longrightarrow H_2SO_5 + H_2O$), and would be stable in acid medium. Explosive reactions of Caro's acid with alcohols have been reported. Its behavior with acetone would probably be similar. It has even been reported to explode spontaneously without addition of organic material.

Preventive Measures:

1. More foolproof identification of wash bottles.
2. Conduct acid digestions behind a safety shield until diluted with water.
3. Dilute digestions before overnight storage.
4. Cover oxidizing materials while standing.

CASE HISTORY NO. 663

Violent Decomposition of Calcium Hypochlorite

Description: Calcium hypochlorite 70% powder for water treatment is received in 100 lb. drums, the contents being added periodically in the required quantity to a 25 gallon crock of water by means of a metal scoop.

The operator whose duty it was to add the chemical lifted the cover off the drum (containing about 15 lbs.) to ascertain how much was on hand. As he lifted the lid he noticed the bed of powder in the drum rising rapidly and, sensing something amiss, he turned away and proceeded quickly about 10 feet to a water hose. While he was turning on the water, the contents of the drum erupted and burst into bright blue flame. Water was immediately sprayed into the open drum and the flame was extinguished. Other than loss of the chemical involved, no damage was sustained; no one was injured.

Cause: When not in use, the scoop was kept in the drum. It was thought that in this way grease, oil or water, or all three, had been introduced into and reacted with the chemical. It was noted also that the metal scoop had a soldered joint which may have also produced a reaction.

Preventive Measures: The metal scoop has been replaced by one of plastic which is not kept in the drum. A platform has been provided for the drum so moisture cannot collect underneath. Operators are now required to wear goggles, rubber apron and rubber gloves when handling calcium hypochlorite. A change to the use of a liquid chemical for easier handling is also being studied.

CASE HISTORY NO. 664

Gas Explosion Occurs When Starting Up

Description: An explosion and fire occurred during the start-up of a Pilot Plant. The Pilot Plant had been shut down for a period of five days during which time certain maintenance work was done, including the dismantling and cleaning of a filter. In less than one minute after feed gas was cut into the system, on start-up, a violent explosion occurred followed by intensive fire. At the time feed gas was admitted, all feed-line valves were in an open position. No previous pressure tests for leaks had been made. Post explosion investigation disclosed that a feed-line flange near the filter, which had been opened during shut-down maintenance work, had not been properly refitted and was open a quarter of an inch, accounting for the source of gas in the building. The source of ignition was determined to be electric heater bands which were not under an air purge as prescribed. The 40 x 80 ft. galbestos building was completely destroyed, and the three occupants in the building at the time of the explosion received multiple burns, which ultimately caused the death of one of the employees.

Cause: Faulty maintenance work and failure to have an up-to-date written start-up procedure. The system should have been pressure tested using the successive section technique. The electric heater bands should have been under purge since they obtain a temperature higher than that required to ignite the feed gas.

Preventive Measures: Closer supervision will be given to the operation to assure that proper procedures are followed. All maintenance work will be thoroughly inspected and tested prior to starting operation of the system. Better housekeeping to be enforced to eliminate excessive combustible materials in the unit and the elimination of all possible feed gas ignition sources.

CASE HISTORY NO. 665

Inadequate Eye Protection

Description: The operator was standing in front of a caustic tank discussing with his supervisor recently performed maintenance work done on overhead steam piping. Drain pipes from the floor above also ran overhead at this point on way to drainage ditch. While he was looking upward, a drop of corrosive liquid fell between the rim of his hard hat and his safety glasses into his right eye. The burn was sufficiently severe to have resulted in 40 per cent loss of vision in this eye.

Cause: Inadequate caulking around joints in piping and inadequate eye protection.

Preventive Measures: The area under the pipes has been made one in which no employee will go without wearing chemical goggles, a continuous water flush now runs through the overhead drain lines; improved caulking has been applied to joints in the piping.

CASE HISTORY NO. 666

Delayed Chemical Burns-- Phenyl Mercuric Acetate

Description: The contents of a 55 gallon drum containing 50 per cent phenyl mercuric acetate, were stirred with a portable agitator, and approximately 40 gallons of the batch were then pumped from the drum for use elsewhere. The drum sat on a portable scale. The drum-scale-agitator combination was made top-heavy by the removal of the liquid.

An employee came along and attempted to push the scale, and due to its imbalance caused it to topple over, the liquid splashing on and above his low cut shoes. The employee washed his feet with soap and water and changed his socks. Approximately four hours later he reported to First Aid, as inflammation of the feet took place. His feet were again washed with soap and water and a baking soda paste was applied. At 8:40 p.m. he visited the plant physician who again washed his feet and applied mineral spirits. Employee's condition worsened resulting in 14 days lost time.

Cause:

1. The employee who was agitating the liquid failed to remove the agitator from the drum and then cover it.
2. The injured employee did not use protective clothing as prescribed on the batch ticket and failed to right the imbalance of the drum by removing the agitator before pushing the drum scale away.
3. The proper first aid treatment was not known.

Preventive Measures: Newly detailed safety instructions have been issued covering the use of this material, after receiving necessary information from the manufacturer and after analysis of the material.

CASE HISTORY NO. 667

Improper Procedure Used for Tank Entry Results in Fatality

Description: Employee was instructing a fumigating contractor's personnel how to fumigate grain tanks with hydrogen cyanide. The first grain tank had been fumigated for about two hours and the hydrogen cyanide was being reverse-flowed through the grain by means of a fan located outside the tanks. Immediately after finishing lunch, the employee left the group he was with, and entered a tank adjacent to the tank fumigated previously, to lay out the hydrogen cyanide nozzles and hose lines, in preparation for fumigation.

About twenty minutes later, after the employee was missed, he was found lying unconscious in the tank. He was removed immediately and although he received first-aid treatment and medical care, he died several days later.

Cause: The grain storage tanks involved were interconnected by auger feed conveyors and the tank in which the employee was found was inadequately sealed off; the center bin-loading spout was sealed with a burlap bag, and two other spouts were not sealed. Also, the flat steel gates ordinarily used for shutting the grain feed conveyors off from the tanks were not used.

Investigation revealed that the grain in all the storage tanks had been treated previously with other fumigants.

Failure of employee to follow the accepted standard safe practices for tank entry as follows:

(a) Failure to make the necessary gas tests before tank entry.
(b) Failure to wear the necessary personal protection equipment including breathing equipment such as gas mask or air mask.
(c) Failure to apply "buddy system" when working with hydrogen cyanide.

Preventive Measures: Safety procedures for fumigation operations will be re-established for fumigation sales representatives.

As soon as these revised procedures are approved they will be reviewed with all concerned personnel.

CASE HISTORY NO. 668

Tendon Severed by Broken Three-Necked Flask

Description: The injured party was in the process of transferring a mixture of phthalic acid and water (about 3500 gms) from a five liter, three-necked flask to a suction funnel. He was holding the flask in his left hand by one of the joints and reached over to remove a stirrer bearing from the centerjoint. At this point, the injured party realized that he had cut his right hand at the base of the thumb. He was immediately assisted by a fellow worker to the dispensary where the plant physician stitched the cut temporarily before sending him to the hospital. The plant physician's diagnosis that the tendon to the thumb had been severed was confirmed at the hospital and an orthopedic surgeon operated that evening and tied the tendon back together. The injured party was released from the hospital the next morning and was able to return to work.

Cause: An interview with the injured party and witnesses to the accident brought out the following points:

1. Prior to the attempt to filter the phthalic acid-water mixture, the flask had been clamped in an ice bath. As the injured party was tightening the clamp, he heard a pop which he thought came from the bottom of the metal ice bucket. It now seems probable that this pop was caused by the breaking of the joint.

This thesis is supported by the fact that the flask joint broke very easily when the injured party attempted to remove the adapter.

2. The adapter which the injured party was trying to remove was not broken and was apparently well greased. It seems probable that the actual cutting was done by the broken flask joint.

Preventive Measures: 1. When handling flasks of this size and weight, two hands should be used to support the flask. In addition, undue strain should not be put on the glass joints by holding the flask in one hand and tilting it to pour out the contents of the flask.

2. More use should be made of gloves and/or towels when handling large glassware containing large amounts of material.

3. When clamping a large flask by a joint, additional support should be provided at the bottom of the flask. In this case, resting the flask on a cork ring in the bottom of the ice bath might have relieved the strain that resulted in the breaking of the joint.

CASE HISTORY NO. 669

Chloride Stress Corrosion Cracking

Description: An employee of a production department was operating a 6-inch gate valve on top of a 48 x 40 ft. diameter storage tank. The bolts holding the bonnet to the valve broke, as he turned the valve, allowing a 9% caustic solution to spray on the employee. The employee ran down the stairs to the ground and showered in a safety shower. Fortunately he received only minor chemical burns.

Cause: A subsequent investigation revealed the following facts:

1. The gate valve was made of a nickel chromium alloy.

2. The bolts were made of 303 stainless steel.

3. The nuts were made of 304 stainless steel.

4. A laboratory analysis showed that the bolts failed because of "Chloride Stress Corrosion Cracking."

5. The atmosphere is contaminated with chlorides from adjacent processing units. (The level of contamination does not constitute a health hazard.)

Preventive Measures: 1. Discontinue use of stainless steel nuts and bolts in this area.

2. The use of monel or high tensile strength carbon steel nuts and bolts will be instituted.

CASE HISTORY NO. 670

Overhauling Steam Control Valve in Place

Description: Two mechanics were assigned the job of overhauling a six-inch fifty-pound steam control valve in place. The line had been isolated by closing four valves, but the need for venting the pressure had not been foreseen. The employees had removed the studs from the bottom cover plate of the valve and, squatting by the valve, they were rapping the flange to break it loose when it suddenly released. Both men were sprayed with condensate and steam. One, fortunately, sustained only minor burns. The other sustained disability burns about legs and arms.

Cause: Failure to vent pressure.

Preventive Measures: Full acid suits will be worn for breaking into steam or condensate lines unless specific exception is made by supervision and, where practical, vents will be added to steam control valves which are overhauled in place.

CASE HISTORY NO. 671

Unsafe "Tank Entry Procedure"

Description: About midafternoon a loader at the caustic tank car loading rack discovered a fellow worker unconscious in a caustic tank car. One employee dropped an air hose into the tank car and turned the air on slightly in order to put fresh air into the tank car quickly. The plant emergency crew arrived immediately and removed the unconscious employee from the tank car. They started administering oxygen immediately and did so continuously until they reached the hospital. The employee regained consciousness soon after oxygen was administered, but remained in the hospital until the next afternoon and was released in satisfactory condition.

Cause: The victim had entered the tank car to sweep it clear of water after having hosed it for some time. Samples of air taken from the car revealed a gas mixture of 10% oxygen and over 85% nitrogen. Air line mask equipment was permanently located at the tank car loading rack for use when going into tank cars, but was not used by the employee on this occasion. It was apparent upon investigation that this equipment had not been used for a considerable length of time.

Preventive Measures:

1. Air line respiratory equipment should be worn by any person who is required to go inside a tank car.
2. Any person who goes into the tank should be equipped with a life belt with a rope attached to the "D" ring for use in removing the person from the tank car in case of emergency.
3. Someone should be on duty outside the tank car dome to observe the person inside.
4. At least three changes of air in the tank car should be made before allowing someone to go inside.
5. Appropriate disciplinary action should be taken for violation of these procedures.

CASE HISTORY NO. 672

Unsafe Condition Plus Unsafe Act--Injury

Description: A Yard Department laborer was engaged in general duties in the trash dumping area. Another employee operating a Dempster truck backed up to the incinerator and opened the Dempster box to discharge its contents. The Yard Department employee, seeing that the contents were not dumping properly, reached into the opened jaws of the box to free the jammed materials. As he did so, the bucket or box lifting bar which was not properly engaged in the hook, slipped off, dropping the top section of the box, which closed the box as tightly as the accumulated trash would permit and trapped the employee's hand.

The employee suffered lacerations of the thumb and palm of his left hand. Fracture first phalanx left thumb, fracture second and third metacarpal bones. Also laceration of back of left hand and second finger on right hand.

Cause:

1. The latching hood was apparently not properly engaged during the dumping operation. The spring mechanism, which positions the latching hook apparently did not provide adequate tension for positive hook-up to the Dempster box bail or lifting bar.
2. Exposure of body or its parts to pinching action of the closing Dempster box.
3. Lifting bar or bail on Dempster box was bent.
4. Operators are not accepting personal responsibility for safety in the operation of equipment.

Preventive Measures:

1. Stronger springs were installed to insure complete exposure of the latching hook for a positive hook-up of the box lifting bar or bail.
2. Employees have been reinstructed to keep the body or any of its parts completely away from the box when in a suspended position.
3. Dempster boxes with bent hooks are not to be used.
4. Make operators conscious of their personal responsibility for safety by:
   a. Making sure the bail is properly latched before lowering the boom.
   b. Making sure that no one is close around box or bucket when it is suspended.
   c. Lowering box to ground for dislodging of materials or cleaning when necessary.
   d. Daily check and reporting on condition of equipment.
5. Appropriate disciplinary action for violation of these procedures.

CASE HISTORY NO. 673

Lockout Procedure not Used

Description: A horizontal conveyor, with slowly moving parts (approx. one r.p.m.) was overloaded with resin at one of its transfer points, and it became necessary to remove a baffle. A mechanic familiar with the equipment, tried to loosen two bolts on the baffle while the equipment was still operating. His wrench caught between the conveyor screw and conveyor housing. This acted similar to a vice and his right ring finger was jammed between his wrench and the conveyor housing.

A positive disconnect switch, installed as a protective device on this equipment, allowed it to be shut down quickly and safely, but was not used.

Cause: The immediate cause of this accident was the worker's disregard of the safety rule to shut down and lock out moving equipment before working on it. The man apparently decided to take a chance even though there was no reason the equipment could not have been shut down.

Preventive Measures: This accident points up need for greater emphasis on individual training and increased safety contact between the supervisor and his men.

1. Meetings of Operating Supervision and the Maintenance Department were held immediately to once again emphasize the mandatory aspects of the Lockout Procedure.

2. Department Safety Meetings during June will have the Lockout Procedure as their main topic.

3. Increase supervisor-worker safety training contact both on a formal and informal individual basis.

CASE HISTORY NO. 674

Minor Explosion in Handling of Chopped Rubber

Description: A minor explosion occurred during the loading of chopped rubber into a dissolving tank. A 75-lb bale of chopped rubber was being loaded into the dissolving tank through a coarse screen by an operator wearing gloves and gum rubber soled shoes. There were no injuries and no damage to the processing equipment.

Cause: It is believed that this explosion was caused by ignition of styrene vapors escaping from the mouth of the rubber charging funnel. Measurements made with field voltmeter adapted to electrostatic measurements indicated that the operator's body was acquiring a substantial electrical charge by induction from the rubber being handled. The operator thus functioned as a floating conductor, accumulating charge which is surmised to have served as a cause of ignition when he accidentally grounded his body against some grounded metal point.

Preventive Measures: It was determined that both chopping and the rubber heating associated with chopping were involved in the electrical charge generation. The problem was solved by installing a small water spray during chopping, which both cooled the rubber and provided humidity control necessary for rapid drainage of charge.

CASE HISTORY NO. 675

Cut into Line Containing Liquid Bromine

Description: A section of line had been removed between reactor and supply line so the reactor could be repaired. The supply line was double valved with a plugcock and porcelain valve. The plugcock was frozen in the open position, and the porcelain valve was in the closed position. To prevent leaks, the open end of the porcelain valve was blanked with a pigtail (a length of lead pipe sealed on one end with a four bolt ring flange on the other end). The employee used a hacksaw to saw the end of the lead pipe to drain it. Static pressure in the pigtail caused a small quantity of bromine to spray onto the man.

Cause:

1. The plugcock was in an open position.
2. The porcelain valve leaked.
3. Pigtail contained bromine under static pressure.
4. Failure to wear adequate protective equipment. (Employee was wearing sideshield safety glasses.)
5. The employee bent the pigtail upward and then hacksawed the end of it at eye level on the side towards his face.

Preventive Measures:

1. Better job planning by supervision and employees stressing:
   a. Hazards of opening or cutting into lines.
   b. Proper position of employee in relation to equipment when opening lines.
   c. Adequate personal protective equipment.

2. The use of pigtails and blanks for other type jobs will be evaluated.

   a. The pigtail for this job will be left open and extended into a neutralizing container.

CASE HISTORY NO. 676

Accidental Ignition of Flammable Liquid in Laboratory

Description: A chemist was working at a laboratory hood preparing a reduction reaction using lithium aluminum hydride. A companion chemist had just left the lab when he heard a cry for help. As he turned back to the lab, he found it in flames and the injured man trying to get out through the door which opened inwards. When the door was opened, the injured man was squeezed between it and the hood.

In his fright, the injured man might have run but fortunately, someone had already pulled a safety shower under which he was led to extinguish the flames and wash the solvent and chemicals from his body.

A first aid fire blanket from the lab was used to wrap the burned man to try to keep him warm until the ambulance arrived. He received first degree burns on his face, and more severe burns on his hands and legs.

Cause: The laboratory door opens inward forming a trap in an emergency. The laboratory contained nearly 100 gallons of flammable solvents in glass bottles and safety cans on shelves. It appeared to be cluttered and overcrowded and hoods were located behind doors.

We believe that the injured chemist was pouring ether (which had been dried over calcium hydride) into a flask containing lithium aluminum hydride. Something caused the ether to flash--a static spark, moisture on the lithium aluminum hydride, or something else. He jumped back from the fire because his face was seared and may have been temporarily blinded. Perhaps there was some ether on his hands which also flashed causing him to drop the bottle containing the ether and calcium hydride. This ether also flashed causing burns to his legs.

Preventive Measures:

1. Despite the apparent inconvenience of drawing solvents and chemicals from a general stockroom, all unnecessary flammable solvents and chemicals should be removed from laboratories and drawn as needed. Supervision should enforce this rule.

2. Chemical . Laboratory doors should be arranged to swing outward.

3. While we should do everything to avoid accidents in labs, we should always anticipate the unforeseen by advance emergency planning. Laboratories should be arranged for convenient working conditions and for easy exit in an emergency. Cabinets, files, etc, often clutter a laboratory and should not be placed in a position where they obstruct passageways.

4. Emergency first aid blankets should be provided in convenient locations in laboratory buildings.

CASE HISTORY NO. 677

Distillation of Ethyl Isothiocyanate

Description: A chemist was distilling ethyl isothiocyanate from a mixture of ethyl isothiocyanate and acetone.

He was using a 22 liter flask as a distilling pot into the top of which a glass condenser had been affixed through a rubber stopper. Water was connected to the condenser to provide cooling for the vapors. Two other openings had been made in the rubber stopper of the still pot. One opening, approximately 3/8-in. diameter, was used for the insertion of a glass tube which was connected to an air supply. Air was being bubbled through this tube to provide sufficient agitation in the still pot so that bumping could not occur. The second opening was covered with a cork.

The chemist noted that he needed an increase in water flow to the condenser. Bending down, he reached over the still pot to the water valve adjacent to the condenser. The water valve was located within an inch and slightly above the air valve which was a standard laboratory plug cock valve. As he rotated his hand on the water valve, he struck the air cock which opened causing a jet of high pressure air to be admitted into the still pot. This increase in pressure within the pot blew the loose-fitting cork from the top of the stopper and blew the bottom of the distillation column off the stopper. The ethyl isothiocyanate and acetone mixture was forced out through the two openings and over the face and body of the chemist. Some of the ethyl isothiocyanate went beneath the injured employee's safety glasses and into his eyes. He sustained rather severe chemical burns to his eyes. Other injuries were superficial.

Preventive Measures:

1. The air line should have a pressure relief to prevent the full force of air from being injected into the still pot. This could be accomplished by means of a manometer in the line and a capillary tube in the still pot.

2. Full face shields in addition to safety glasses should be worn around chemical reactions.

3. Control valves should not be so close together that they may be inadvertently actuated.

CASE HISTORY NO. 678

Explosion in Nitrobenzene Recovery Kettle

Description: Nitrobenzene was being recovered in a cast iron jacketed distillation kettle by heating with steam at 90 lbs. pressure and operating under vacuum. After the distillation was complete the kettle contents were inspected for viscosity of the tarry residue. A small amount of nitrobenzene was added to make the mass more liquid prior to blowing contents with inert gas through a bottom outlet valve into drums. Due to other more urgent work, the operator interrupted the above sequence after the kettle had been sealed just prior to the blowing operation. The kettle was held at 150^{O} for about one and one-half hours. Just before the operator was planning to blow the residue out of the kettle, hissing noises of escaping gases were heard. Personnel took cover as best they could and reported that they saw vapors issuing from the main gasket of the kettle. About 4-5 seconds later the kettle ruptured violently and was torn from the steel I-beam floor supports, dropping to the floor below. The cover was ruptured into many parts; some pieces were found 40 ft. from the scene. All windows except those directly behind the kettle opened automatically at the spring loaded latches thus relieving a great deal of the pressure and greatly minimizing glass breakage.

Fortunately there were no injuries to personnel and damage to adjacent equipment was of a minor nature.

Cause: A detailed investigation by both the manufacturing and research laboratory personnel revealed the following:

1. Shortly after the accident a similar condition was in the making in an adjacent nitrobenzene recovery kettle. This could be kept from getting out of complete control.

2. Residues from the kettle which exploded showed an acid analysis of 5-30% determined as sulfate.

3. The receiver which contained the distilled nitrobenzene contained large amounts of sulfur dioxide.

4. The contents of the second-mentioned kettle showed large amounts of acid present.

It has always been the practice to wash with 5% sulfuric acid all nitrobenzene known to be contaminated with amines before carrying out the vacuum distillation. Later it was determined that when the nitrobenzene is charged into the washing kettle first, followed by sulfuric acid and then water, that an emulsion layer frequently results and that sulfuric acid settles to the bottom of the kettle in spite of vigorous agitation. If the water is charged first followed by the sulfuric acid and then the nitrobenzene, emulsions are not formed and the acid layer is on top of the nitrobenzene.

It is apparent that acid-containing nitrobenzene got into the cast iron distillation kettle. Under these conditions, hydrogen was generated. The explosion was caused by either hydrogen alone or unstable intermediate reduction products of nitrobenzene or a combination of the two.

Preventive Measures: To prevent a recurrence in the future, the method of washing with dilute acid will be changed as indicated above and as an extra precaution a dilute soda ash wash will be given prior to the vacuum distillation. Furthermore, strict instructions have been given that no time should elapse from the time a distillation is complete until the tar is blown out. To avoid opening the kettle after the distillation is complete, an ammeter will be installed on the kettle to show the proper end point.

In view of the two recent serious accidents involving nitrobenzene and acid in this country and a similar one in Germany, our affiliated firm has undertaken a detailed research project on this matter. It is recommended that all firms using nitrobenzene review their operating procedures and that the MCA re-examine the Safety Data Sheets on Nitrobenzene.

(Editor's note: The General Safety Committee of MCA will follow this recommendation to review SD-21 Nitrobenzene and will issue a revision if such is shown to be necessary.)

CASE HISTORY NO. 679

Unsafe "Fail Safe"

Description: An inert gas generator is used at the plant to maintain an inert atmosphere in equipment and bins where finely divided resinous material is handled.

The gas generator burns natural gas under carefully controlled conditions. Combustion gases pass through a scrubber and then through a compressor into a holding tank at about 90 psi. The combustion chamber is provided with a flame safety device and the gas supply line from holding tank to equipment is provided with oxygen analyzing equipment.

Although the flame safety device was of "fail safe" design, failure did occur which permitted the unburned gas-air mixture to enter the holding tank and from this tank into equipment.

The oxygen analyzing equipment gave warning and resulted in a shutdown when oxygen in some equipment had reached 5 per cent. Recorder charts indicate that the mixture in the holding tank was within the flammability limits.

Preventive Measures: This incident indicates the necessity of "back-up" devices even though the primary safety control is "fail safe". In this case an additional oxygen analyzer monitoring the gas entering the holding tank is being provided.

CASE HISTORY NO. 680

Unexpected, Uncontrolled Reaction

Description: Reaction of chlorinated compound, caustic soda and water went out of control when delayed reaction temperature reached 40°C. above normal operating temperature. No injury--no plant damage.

Discussion and Speculation: Method of caustic addition while heating to reaction temperature permitted delayed reaction which went faster than expected when reaction temperature was reached. This permitted the temperature to reach a critical point beyond which control was not effected.

Operation of relief valve resulted in loss of batch through vent. Relief valve setting was consistent with design pressure of the reactor (1,000 pounds) rather than to accommodate the reaction (130 pounds), therefore, control through venting was not obtained at lower pressures.

Preventive Measures:

1. Determine the dividing line between safe and unsafe reaction temperatures.
2. Establish temperature and pressure points for manual venting to control the process.
3. Lower relief valve setting to near normal reaction pressure.
4. Add caustic at reaction temperature.

CASE HISTORY NO. 681

Laboratory Glass Injury

Description: A laboratory analyst was given a phosphorus ore to analyze. This particular type of sample had never been analyzed in this laboratory; hence, the head of the laboratory gave a full explanation of the method being used to the party assigned to the job.

He proceeded to fill his burette with the standardized caustic solution, which was in a 250 ml. volumetric flask. Then, in order to take the burette reading, he raised himself with the help of a laboratory stool and while he was reading the burette, he tried to stopper the flask at the same time and without looking. Since an oversize stopper was being used, the flask was not properly stoppered; and therefore, when the analyst saw this he tried to force the stopper in by hitting it "lightly" with the palm of his right hand, but as the impact was too much for the stem of the flask, it broke immediately, leaving a pointed edge that cut the analyst's right hand deeply. He began bleeding profusely, and tried to stop the bleeding by putting his fingers on the wound; while this was taking place, a fellow analyst took a piece of cotton which he immediately used to press against the injured point. Since all this did not stop the hemorrhage, the injured analyst was taken to the infirmary for treatment. The doctor cleaned and sterilized the injury, and then proceeded to stitch the cut, which necessitated six stitches.

Cause: The main cause of the accident was carelessness of the analyst, and lack of sufficient equipment for non-routine tests, as well as inadequate use of existing equipment.

Preventive Measures:

1. Laboratory should acquire enough equipment to run non-routine tests and maintain the existing equipment in good working conditions. The Laboratory Supervisor to be responsible.
2. Review with all laboratory personnel all the working procedures, and especially the need to have the necessary equipment to perform the routine and non-routine tests. The Laboratory Supervisor to be responsible.

CASE HISTORY NO. 682

Accident Transferring Cyclohexylamine from Drums

Description: An operator began to unload his second drum of cyclo-hexylamine after coming on shift at 3:00 p.m. Cyclo-hexylamine drums are brought up to the third floor of the Organics Building, where they are weighed and a predetermined amount (approximately three drums) is transferred to a charge tank located on the second floor level, over the kettle in which it is used. The drum is manhandled onto a platform scale and, after weighing, a dip pipe assembly is screwed in the bunghole. This assembly consists in part of a dip pipe which extends to the bottom of the drum and has an "evertite" fitting on top for connection to a short length of 1-inch chemical rubber hose, which in turn goes to the transfer line to the cyclo-hexylamine hold tank. In addition to the dip pipe, there is another connection on the assembly which is used to pad the drum with 2 psig. air pressure, to initiate the syphon flow.

Standard operation of transferring the cyclo-hexylamine consists of the following steps:

1. Place the drum on the scale and remove the bung fitting and screw in the dip pipe assembly.

2. Connect the cyclo-hexylamine transfer line with the "evertite" coupling and open the valve in this line.

3. Connect the air line to the other "evertite" coupling.

4. Open the air line valve before the pressure regulator. Observe the air pressure before opening the second valve and admitting air to the drum.

5. After flow has started, the air supply to the drum is shut off using both valves, and the vent petcock is opened and the balance of the material is transferred by the syphon effect.

The operator had placed the drum on the scale, and screwed in the dip pipe assembly. Since some difficulty was encountered in placing the drum in the proper position to connect the air line, due to the inflexibility of the hose used, he partially inserted the air line to see if it could later be connected in that position. At this time, the cyclo-hexylamine line had not been connected. Upon insertion of the air line, he noticed the cyclo-hexylamine rise in the dip pipe and he instinctively tightened his grip, which served to clamp the air line in place, and at the same time averted his head to the left. The cyclo-hexylamine spurted out of the dip pipe, splashed off the top of the drum and onto the right side of his face. Safety glasses were on at this time and no material splashed into his eye. However, in his subsequent attempt to get to the safety shower, which was located approximately thirty feet away, he opened his right eye and some cyclo-hexylamine ran in, causing damage to the interior of the eyelid and the transparent tissue over the cornea, in addition to the burns already suffered on the right side of his face.

Cause: The decision to try the air hose without completing the prior steps of the connection instruction was the principal cause. The injured operator had already transferred one drum and had been lax in shutting off the air valve after the first drum. No valve leakage was detected on subsequent examination and this was not considered to be a contributory factor. The operator had had a previous encounter with this material from a leak dropping on his leg and should have been more cautious.

However, the use of air pressure to initiate or maintain liquid transfer from drums is prone to such mis-operation and should be discontinued, especially on hazardous liquids.

Preventive Measures:

1. All operators have been re-instructed on the proper unloading procedure. Any addition to these instructions should be rewritten to incorporate the necessary safety equipment to be worn for the job, and the hazards of the material are to be emphasized.

2. The use of a face shield and #710 type safety goggles should be made mandatory until the present set-up can be changed.

3. The rubber hoses, which are attacked by cyclo-hexylamine, should be discarded and replaced with another hose (such as tygon) which is not attacked. This will reduce the hazard from spills due to hose failure.

4. Every operating department should re-appraise all plant operations involving the handling of hazardous liquids in drums, and the prescribed safety equipment should be included in any operational write-ups.

Editor's note: Publication of Case History No. 682 brought comment from a member of the MCA General Safety Committee that "the only thing which seems to concern the company which submitted this case history is the fact that the operator got a squirt in the eye. They completely overlooked the extremely important fact," he continued, "that flammable liquids should never be transferred by use of compressed air."

The reply of the safety director of the company which submitted the case history points out that the report as published in our January issue should have, but did not, clearly indicate that the air-pressure method of unloading flammable liquids from drums has been discontinued. He states as follows:

"When this accident was originally reported to our office, I telephoned the plant safety engineer because I, too, was disturbed to find that flammable liquid was being unloaded by air pressure. He said that they had discontinued the use of air pressure and were now using a pump and that this was covered by the paragraph immediately preceding the "Preventive Measures" section of the MCA report which states, 'However, the use of air pressure to initiate or maintain liquid transfer from drums is prone to such mis-operation and should be discontinued, especially on hazardous liquids.' He further stated that Item #1 of "Preventive Measures" which reads 'All operators have been re-instructed on the proper unloading procedure' meant that the 'proper' unloading procedure was by pump. Item #2 under "Preventive Measures" indicates that certain protective equipment should be worn until the present set-up could be changed. By the time we received this report, the set-up had been changed to pump rather than blow drums."

CASE HISTORY NO. 683

Fatal Accident Involving Fluoride Mixture in Steel Cylinder

Description: Several hundred grams of crude reaction mixture involving nitrogen trifluoride and tetrafluorohydrazine had been collected three days prior to the incident in a small stainless steel cylinder. During the opening of valves to measure the cylinder's pressure by means of an attached pressure gauge, the cylinder ruptured with considerable force and was torn into three pieces. The exact cause has not yet been completely established. A fireball of exploding gas filled a one-story room, blowing out windows and loosening some cinder blocks in the walls. A technical trainee who was opening the valves received the full force of the blast and died from multiple internal injuries. An engineer who was in the same room was knocked down and sustained a fractured leg and a perforated eardrum.

Cause: Not yet completely determined.

Preventive Measures: The operation will be barricaded and operated by remote control.

CASE HISTORY NO. 684

Fatal Accident with Elevator Hoist

Description: A centrifugal discharge bucket coal elevator had been used on the night shift to unload coal from RR cars to the bunkers located at the top of the power house. The excessive amounts of wet coal falling off the buckets caused the buckets to become wedged in the boot of the elevator. On the next shift (day) an attempt was made to clean out the coal to free the buckets so the elevator could be put back in use. Before attempting any cleaning the fuses were pulled and a. safety hold card was placed on the disconnect switch. Normal procedure for freeing the elevator was to open the clean-out door on the front at the base of the elevator housing and remove the coal with the proper tools. Three men were engaged in freeing the elevator. Two of the men went to the third floor to inspect the coal chutes to see if they were clogged, leaving the one man at the base door cleaning out the coal. When the two men returned to the basement from the third floor they noticed the other man had his head in a small chute opening on the side of the elevator. On calling to him and receiving no response, closer examination disclosed the man's head caught between the elevator bucket and the side of the housing opening. The man was dead on removal. It was determined that at the exact time the man placed his head in the chute opening, the elevator moved back due to the weight of the loaded buckets on the up-take side of the elevator. No reason could be determined as to why the man placed his head in the opening.

Preventive Measures: A metal grid will be welded over the chute openings allowing only numerous 3-inch openings. Other areas of the plant will be inspected for openings similar to this type and protective measures will be taken where needed.

CASE HISTORY NO. 685

Anhydrous Ammonia Burn from Hose Rupture

Description: The truck driver of an outside concern to whom refrigeration grade anhydrous ammonia is sold, after having weighed in on the plant scale, backed up to the loading area. The gauge on the truck showed 90 psi since the tanks are never completely emptied. A raw material handler connected a special stainless steel flexible hose to the common header valve of this truck and then, by use of a half union, to the outlet valve on the storage tank. The truck driver opened the valve on his truck and the handler then started to open the valve from the storage tank. Almost immediately, the flexible hose ruptured close to the inlet valve of the truck tank. The handler then closed the tank valve. The ammonia in the truck tank started to escape and the foreman put on a complete rubber suit and a Chemox mask and shut off the valve at the tank truck.

While performing this job, he received a burn on his right forearm from either the impingement of the anhydrous ammonia against the rubber suit or vapors which condensed between the rubber suit and the gauntlet gloves. The area was then washed down. The truck was re-weighed and showed a loss of 2,500 pounds.

The flexible hose used is purchased according to specifications: 6 ft. x 1-1/4-in. seamless steel braided flexible hose, 1,200# bursting pressure, with extra heavy 1-1/4-in. pipe nipples welded to each end. No copper or brazing permitted.

Cause: Rupture of flexible hose.

Preventive Measures: 1. Install 200# check valve on tank truck line.

2. Raw material handlers to wear full head and face protection while operating valves.

3. Consider use of impervious suit for emergencies.

CASE HISTORY NO. 686

Chemical Irritation of Both Eyes

Description: Employee was exposed to two potential eye irritation incidents as follows: First, approximately 75 lbs. of diethyl chlorothiophosphate spilled from a hose on to the working platform during transfer from a reaction vessel to a hold tank. The injured employee put on his gas mask immediately and with another employee cleaned up the spill.

About an hour and a half later a mechanical seal on an organic phosphate acid pump failed and approximately 75 gallons of the acid spilled on the floor. The employee stayed in the area until the area was secured and then put on a gas mask and cleaned up the spill with the assistance of another employee. Some time later the injured employee reported to the Medical Department.

Cause: Hose connection to storage tank had not been tightened and diethyl chlorothiophosphate spilled through the loose connection.

Failure of mechanical seal on the pump to hold due to entrained solids in the organic phosphate acid, and failure of the employee to put on eye protection immediately at the time the exposure occurred.

Preventive Measures: 1. A method of filtering the solids from the acids is presently being investigated and will be installed as soon as determined.

2. Employees will wear gas masks or air masks when starting up organic phosphate acid pumps and continue to wear the eye protection until certain that the pump is operating normally.

3. Employees were instructed to make sure that hose connections are tight before making product transfers.

CASE HISTORY NO. 687

Faulty Valves and Lack of Eye Protection

Description: An employee was filling a cavity in front of #6 Sulfur Furnace with a type of acid cement. This was being pumped under 20 pounds pressure. He shut off the pump and opened a relief valve in the line to bleed off the pressure. This was done so that he could break the line at a union near the front of the furnace. As he attempted to break the line, the material sprayed out hitting him in the eyes and face. He was not wearing eye protection and the cement entered his eyes causing severe abrasions of both corneas with severe conjunctivitis secondary to the injury.

Cause: Investigation revealed that the nipple on the relief valve was frozen shut and failed to bleed off the pressure when it was opened. Also a valve ahead of the union could not be completely closed because of the cement setting up on the valve seat. As a result of these two valve failures, line pressure was on the union when he cracked it allowing the material to spray out.

Preventive Measures: 1. Employees have been informed of this accident and again instructed to wear eye protection.

2. During cold weather valves will be kept warm and operable with the use of propane heaters.

CASE HISTORY NO. 688

Electrostatic Spark Ignites Toluene Vapor

Description: An employee was transferring toluene by vacuum from a 55 gallon drum to a kettle through a one-quarter inch plastic tube. The tubing at the drum end was fitted with a flannel filter (held in place by two turns of copper wire) in order to prevent contamination of the kettle with scale from the drum. When the desired amount of toluene had been transferred, the employee pulled the tube from the drum. At this time, vapors ignited and enveloped the area around the bung opening of the drum. The employee received moderate burns on the left wrist and hand.

Cause: A thorough investigation after the fire revealed the following facts:

1. The toluene drum was not grounded.
2. The copper wire holding the flannel in place had two antenna-like projections.
3. Both ends of the drum were bulged after the fire.
4. Plastic tubing is a nonconductor of static charges.
5. The toluene drum was one quarter full after transfer was made.

From the above facts, the following conclusions were made:

1. As the toluene passed through the plastic tube, a static charge was built up on the tube.

2. The static charge collected on the antenna-like projections of the copper wire.

3. The toluene vapors around the bung opening of the drum were within their explosive limits.

4. As the tube was pulled from the drum, there was a static discharge, with a spark, from the copper wire to the edge of the bung opening of the drum, causing ignition of the toluene vapors. This in turn was followed by a flash fire outside the drum and an explosion inside the drum.

5. Had the drum ruptured, the accident would have resulted in a much more serious fire and injury.

Preventive Measures: 1. Transfer tubes will be made of stainless steel and grounded.

2. Operators will be reinstructed to make sure the grounds on the kettle and drums are secure.

CASE HISTORY NO. 689

Splashed with Molten Phenol and Hot Water

Description: At 11:30 p.m., the phenol department fusion operator tapped out the west finisher. The west fusion pot was tapped at 11:45. The tap-out cocks were closed when the vessels stopped draining and wash water was pumped into the fusion pot. The operator visually inspected the finisher before putting in water to check for the presence of excess fusion mass. Everything seemed normal so the finisher was filled with water to the overflow. The head operator was present during these operations in case of an emergency. When the finisher was full, the head operator started to turn off the flow of water and the fusion operator turned to go to the deck below. At this point, the finisher erupted and a mixture of fusion mass and water gushed out the hatch of the finisher, spraying the two operators. This happened approximately one hour after tapping out the finisher.

Cause: The cause may be attributed to:

1. Too much fusion mass remaining in the finisher so that when the water finally worked through the crust on top of the mass and started to disssolve it, the volume of steam liberated at the bottom of the vessel pushed the contents out at the top.

2. The fusion mass and the finisher were too hot, contributing to the formation of steam.

3. The vessel was full of water leaving no space for the steam to disengage from the water.

Preventive Measures: 1. Operators will be reinstructed to allow the finisher to cool for approximately two hours after tapping before adding wash water.

2. Operating instructions will be revised to read: "Fill only one third full, with the agitator running while filling, and mix thoroughly before continuing washing procedure."

CASE HISTORY NO. 690

Respiratory Irritation--Sulfur Dichloride

Description: Sulfur dichloride is charged to the Actamer process by sucking from drums into the reactor. Each drum, either full or partially full, is spotted on a scale, a vent hood is placed over the side bung, and the plug is loosened to vent any pressure build-up.

The operator loosened the plug of a part drum at about 9:40 a.m. He then proceeded with other duties. Twenty minutes later, after the drum had apparently vented, he reached under the hood and removed the plug. As he did, sulfur dichloride fumes escaped in his face.

The immediate respiratory irritation and shock from the fumes drove him to the floor. He crawled to the east side of the area where he tried to attract the attention of someone on the lower level. Unsuccessful in this, he eventually made his way to the ground floor and was assisted to the dispensary for treatment.

He was released from the dispensary at 3:15 p.m.

Cause: Sulfur dichloride is a heavy fuming liquid with a boiling point of 59°C. It reacts violently with water and decomposes readily above 40°C. It is a severe respiratory and eye irritant even at very low vapor concentrations.

Drums of sulfur dichloride are stored indoors on the third level where ambient temperatures are high enough to cause some decomposition. Partly-filled drums are particularly hazardous on account of the moisture in the air in the free space.

The pressure build-up in the drum involved in this incident resulted either from thermal decomposition of sulfur dichloride or from reaction with water in the air. The bung plug reseated itself after being loosened and permitted a pressure build-up. The gas evolution when the drum was opened was too great to be removed by the vent hood.

The vent hood consists of a small cone attached to a three-inch flexible hose in the blower system. The suction pipe for unloading is inserted through a hole in the cone. The arrangement is awkward in the close operating quarters and fits the drum too loosely to vent effectively.

The injured was wearing goggles and gloves at the time of the incident. Operating instructions specify an apron and organic respirator, also. Although a respirator might reduce the severity of exposure to sulfur dichloride, it would not give adequate protection. Only an independent air supply can be relied upon to do this.

Preventive Measures: The committee recommends action on the three contributing factors to this incident.

Departmental:

1. Drum Storage – Design a drum cooler adequate for at least two drums of SCl_2 or other volatile materials. Until cooler is operable, all full or part drums of SCl_2 are to be stored out of doors.
2. Vent Hood – Supervision to supply area maintenance with a design for an improved vent hood.
3. Personal Protection –
   a. Select a supplied-air respirator system with a fixed cylinder and hose extension for use in the area.
   b. Operating instructions should be amended to exclude use of chemical cartridge respirators as protection for sulfur chlorides since they are not recommended regardless of concentration or time of exposure. Amended instructions to be effective upon installation of the "supplied-air" system.

Plant-Wide: All department supervisors to review their procedures and equipment for handling drums of SCl_2 and other similarly hazardous materials. Check, in particular, the type of respirator recommended by operating instructions, and its effectiveness with the specific materials handled.

CASE HISTORY NO. 691

Communication Failure and Failure to Follow Established Standard Safe Practice

Description: A very serious accident potential developed in one of our operating departments on Friday, February 24, 1961. Two men received second degree splash burns; one more extensively than the other. It was a very narrow margin by which both men escaped fatal injury. It was planned to enter a large stock tank (10 ft. x 20 ft. x 10 ft. deep) to remove a deflector plate under an inlet pipe which drains into the tank, and replace it with an elbow. The stock tank receives the contents of a completed pulper operation. The temperature of the pulper approximates that of boiling water. Therefore, it is normal and necessary to pre-plan what safety measures are to be taken to insure that the hot material from the pulper is not dumped into the stock tank while men are inside it.

Cause: The operation was discussed by supervision of both the operating and field department. It was agreed that since this particular tank received only material from one pulper, that the work could be done safely if the entire system was shut down and empty. Due to communication failure, delegation of responsibility, and an unavoidable absence of one supervisor, no supervision was present in the immediate work area when two mechanics reported to start work. The two men did make an effort to insure their safety by questioning two operating department people who, not knowing conditions, were not in a position to help or advise.

A ladder was then inserted into the empty tank to enable them to climb down to start work. Moments later they heard a gurgling in the inlet pipe and recognized its significance. By desperate efforts they were able to escape up the ladder. If for any reason the ladder had been moved away from the tank manhole, it would have been impossible to reposition it to escape. The result: death by scalding.

Preventive Measures: The communications failure and failure to follow established safe practices has resulted in the following recommendations:

Whenever work is planned in any one of several of this type stock tank, the inlet pipe will be disconnected and a blank cover installed on the pulper outlet end to insure complete cutoff. A "Work Permit" system has been recommended. This would apply whenever it is required to enter a definite confined area. This permit would require the signatures of all parties concerned in any given work operation. The provisions and requirements of a work permit system together with adherence to our Safe Practice Standard, will definitely prevent a recurrence.

CASE HISTORY NO. 692

Exposure to Chlorine Gas

Description: A structural failure occurred in a reactor column, causing a section of the shell, complete with brick lining, to collapse.

This allowed an escape of chlorine gas to the atmosphere, contaminating the area. The employee, attempting to put on a Chemox mask while still in the building, encountered difficulty in getting the mask to operate due mainly to the fact that he had already been exposed and was in no condition to wear a mask.

The employee returned to work next day but was consequently disabled due to after effects.

Cause: Attempting to put on a Chemox self contained breathing apparatus while in a contaminated area and also, after having been exposed to chlorine gas.

Preventive Measures:

1. Emphasize re-training of personnel on this apparatus where necessary to ensure complete familiarity in an emergency.
2. Re-emphasize that this apparatus must be charged (put into operation) in an area that is free from gas.

CASE HISTORY NO. 693

Sodium Methylate and Chloroform--Violent Reaction

Description: The chemist involved in the explosion stated that he was attempting to prepare methyl ortho formate, which in turn was to be used in acetal synthesis. He was using a general method, very loosely outlined in "Synthetic Organic Chemistry" by Wagner and Zook. He stated that he had mixed 270 grams of sodium methylate with 1 liter of methanol and 200 grams of chloroform in a two-liter flask. The flask was put in the water bath. Very shortly thereafter, the reaction began to boil. At this point he dropped the flask into the bath and stepped backward about two feet. A violent explosion occurred in the bath almost immediately. The bath walls contained the force of the explosion, directing the force upward through the opening at the top of the bath. The wall of the bath ruptured slightly. The recoil of the bath fractured the alberene stone desk top. The contents of the bath and flask (approximately five gallons of water in bath) were blown upward to the ceiling and rained down. The chemist suffered minor alkali burns on throat. He immediately flushed face and neck with water to remove alkali.

Cause: An article was found by the investigating group describing the preparation in detail. The article states that the chloroform and methanol are mixed and sodium metal is added slowly over a 2-hour period with cooling. Other references state that sodium methylate may be used instead of sodium metal.

It is the conclusion of the investigating group that the explosion was caused by addition of all of the sodium methylate at one time rather than adding it slowly. This would tend to give a violent uncontrolled exothermic reaction such as occurred. It is to be noted that none of a half-dozen literature references list this as a dangerous reaction or that precautions are to be taken.

Preventive Measures: As a preventive measure, unfamiliar reactions of this type will be thoroughly studied in the literature before actual trial. Further, if specific details cannot be found to a reaction, the reaction will be tried on a very small scale with proper shielding before going to a relatively large scale.

Editorial Comment: Case History No. 498 shows that if the mutually insoluble mixture (sodium hydroxide and chloroform) is made soluble by the addition of a mutually soluble solvent such as methanol, a vigorous and exothermic reaction may occur.

CASE HISTORY NO. 694

Hydrogen Explosions

Description: Following operating difficulties in a chlorine-manufacturing area, two separate explosions occurred from hydrogen-air mixtures; one in the cooling coils of a compressor and a later one in the low pressure hydrogen holder. No one was injured. A failure of the control system caused a back-pressure to develop in the chlorine-manufacturing system. When operating personnel attempted to shut down the system by manual interlocks, a malfunction of this equipment caused a serious chlorine gas exposure. Since one of the two compressors which take hydrogen (manufactured concurrently with chlorine) from a low pressure holder to the high pressure storage tubes continued to operate, the holder was emptied due to the failure of a low level interlock and a negative pressure developed in the system. Air was sucked in and an explosion occurred in the third stage cooling coils of the compressor. No other damage from this explosion was noted. Hydrogen available from another area was later introduced into the holder in an effort to maintain operations. An air-hydrogen mixture occurred in the holder, diffused back into the catalyst purification unit where high temperature developed almost instantaneously causing a second explosion which ripped off the holder roof and collapsed portions of the floating section side walls.

Cause: Failure of a low level interlock on the low pressure hydrogen holder which did not shut down the second compressor. This occurred because an electrical jumper had been installed on the purge timer. No explanation for this jumper has been determined, although there is the probability that, at some time in the past, there had been trouble with the timer and, unknown to supervision, it was by-passed with this jumper.

Preventive Measures: Install a manual shutdown switch for the hydrogen holder compressor next to the cell emergency shutdown switch so that operators can stop the hydrogen compressors while actively coping with an emergency elsewhere in the area. Functioning of low-level holder interlocks will be checked daily. The holder will also be equipped with a low pressure switch which will automatically shut down the two hydrogen compressors—this switch will act independently of the low level cut-offs and will be checked daily. The consequences of jumping safety devices without permission from supervision has been stressed to all personnel. Under no circumstances will hydrogen be introduced into a system until the cause of abnormal conditions has been determined. The use of the particular catalyst hydrogen purification unit has been discontinued until a positive means can be found to exclude the possibility of air-hydrogen mixtures of explosive range from entering the unit.

CASE HISTORY NO. 695

Eruption of Caustic Solution from Beaker

Description: A laboratory technician was assigned the cleaning of 100 cc polythene beakers used under burettes for adjusting readings. The beaker from the silver nitrate burette had a black stain and thin black deposit on the bottom on which he tried unsuccessfully, in turn, dilute nitric acid, hydrochloric acid, a nitric-hydrochloric mixture, and ammonium hydroxide, rinsing the beaker with water after each attempt. Noting some improvement with the last-named reagent he half-filled the beaker with a 25% caustic soda solution and set it aside. A glass stirring rod remained in the beaker.

On returning from lunch he walked toward the end of the laboratory bench where he had left his safety spectacles. As he passed the beaker he noted it was close to the edge of the bench and pushed it to a safer position. There was a loud report and the liquid erupted, some drops striking his face and eyes.

Cause: An analysis of the black deposit in the beaker indicated the major element present was silver (with small amounts and traces of others), chiefly as silver chloride. A test for azide was negative. Attempts to reproduce the reaction under controlled conditions were unsuccessful. From several references in the literature it would appear that the reaction of ammonia solutions on silver salts in presence or absence of caustic solutions can result in the formation of explosive fulminating silver. It also appears that the treatment of silver salts with aqueous ammonia followed by exposure to air, or the application of heat, is potentially hazardous. An additional consideration is that it has been shown that polythene will adsorb both cations and anions from solutions and it is practically impossible to remove completely the adsorbed cations and anions.

Preventive Measures:

1. Instructions have been issued to use only water for cleaning beakers unless other methods are authorized by the chief Chemist. In the latter event, neither ammonium hydroxide nor caustic solutions will be used to clean beakers stained by silver salts; if necessary such stained beakers will be discarded.

2. Polythene beakers in burette service have been replaced by glass beakers which, due to greater transparency, will facilitate inspection for cleanliness.

3. The entire laboratory has been made an eye protection area rather than certain areas and specific jobs.

CASE HISTORY NO. 696

Buried Truck Driver

Description: At approximately 8:00 a.m. an outside contractor's dump truck was positioned under the ash silo to pick up a load of ashes. The silo is equipped with two air-operated slide gates which work independently of one another to control the flow of ashes. One gate was opened to fill one section of the truck and then closed. When the truck was repositioned the second gate was opened. Apparently, the silo attendant then closed the valve supplying air to the cylinders which operate the slide gates.

Due to this error, the attendant could not close the second gate. When the ashes spilled over the top of the truck body, he shouted a warning to the driver and escaped from the silo through a rear door. The driver attempted to move the truck out but the spillage of ashes under the rear wheels prevented the truck from moving. Using good judgment, he then turned off the motor ignition and shut the cab windows.

The truck was completely buried with the exception of the radiator core. The first approach to rescue the trapped man was made by attempting to pull the truck out from under the heavy weight of the ashes using a steel cable attached to a railroad engine and the front axle assembly of the truck. A second attempt was made using a one-man operated mobile truck crane using the same hookup arrangement. Both attempts failed.

A large sheet of plywood was then used to divert the flow of ashes away from the front end of the truck. This allowed the rescue team to clear a path to the truck windshield and momentarily introduce a flow of bottled oxygen into the truck cab after breaking out one section of the split windshield assembly. The driver climbed out apparently suffering no ill effects. To minimize shock, he was placed on a stretcher and taken by ambulance to the Medical Dept. An examination did not disclose any injury.

The rescue was effected in approximately 25 minutes. It is fortunate that the driver was inside the truck cab which no doubt received some natural air movement through the radiator core up into the cab proper.

Preventive Measures: The air supply control valve will be located on the outside wall of the silo. Also, openings will be cut into the enclosure wall directly opposite the control valve handles. This arrangement will insure access to the gate controls and prevent a recurrence.

The recommendation for the driver to remain in his cab will still remain in effect.

CASE HISTORY NO. 697

Man Struck by Falling Roll of Paper

Description: The paper handler was struck by a falling roll of paper stock weighing about 700 pounds and thrown to the floor from a seven foot platform.

The worker's duties included removing test samples from rolls of paper stock. The rolls of paper are hung in vertical racks about 13 feet high. Each rack holds four rolls of paper, one above the other.

Using a rolling platform equipped with a ship's ladder and double rail, the employee cut the paper end coverings from the top roll on the rack. To do this, it was necessary for him to stand on the intermediate rail of the platform. Even at this height, it was difficult to check the roll to make certain that it was hung properly. (Employees have been instructed not to touch rolls that are not hung properly.)

As the roll was touched or rotated, the pipe rod supporting the roll slipped from one end of the rack. The roll of paper dropped, struck the rail of the platform and fell end-over-end down the steps to the floor. The falling roll knocked the employee to the floor where he apparently struck his head against one of the steel channels which serve as guides for the roll handling trucks.

Present information indicates that the employee received severe body bruises and a head laceration.

Cause: This accident reveals several weaknesses in the handling of rolls, namely:

1. There is no positive method provided to insure that the roll handling truck is in proper position to hang the rolls of paper. In 1952, holes were installed in the guide rails to position the trucks. They proved to be unsatisfactory and their use was discontinued.

2. The roll truck operator cannot see whether or not a roll is being hung correctly as his view is blocked by other rolls of paper on the racks and the roll of paper being hung.

3. After hanging the roll, the truck operator did not check it to see that it was properly hung or if it was later "bumped" from its support by another roll of paper.

4. The injured man did not use the high platform rack that is provided.

5. The injured man did not check to make certain that the roll was properly hung before he attempted to remove a sample.

Preventive Measures: The Industrial Safety Dept., the Engineering Dept., and the operating department are mutually working on plans to insure proper hanging of rolls of paper.

CASE HISTORY NO. 698

Back Injury--Cleaning Filter Press

Description: Employee was cleaning a Schriver 24 x 24 inch iron plate and frame filter press. He was working alone. As this employee attempted to slide the cleaned plate up the rails and out of his way, he jerked too hard on one handle of the plate, causing it to jump the rail and to fall. He grabbed at it as it fell and tried to hold on.

These plates weigh about 108 pounds. The position in which he was standing at the time, put an unusual strain on his back while it was in a twisted position. The accident resulted in a severe back injury which ultimately required surgery.

Cause:

1. The position this employee was required to take while sliding one of these rather heavy plates up the rails on the filter press frame, resulted in a dangerous torque type of a strain to his back.

2. This type of plate normally is equipped with a small knob-like protrusion located

on the under-side of each of the plate handles so designed as to prevent the plate from jumping the side rails. This knob had been broken off and this condition was unobserved by the employee.

3. The employee involved in this incident had a congenital back deformity making him particularly susceptible to this type of an injury.

4. Because of his having had previous episodes of back pain, this employee had been instructed by his physician to wear a back brace while at work. At the time of the incident, he was not wearing this brace.

Preventive Measures:

1. The rule that two men will be required for cleaning and/or assembling any iron plate and frame filter press having plates 18 inches square or larger, has been agreed upon and put in practice.

2. All filter presses of this type have been reinspected in order to make sure that they are not defective.

3. Greater effort has been made to control job assignments for employees having known physical limitations to the end that job requirements will not be inconsistent with physical capabilities.

CASE HISTORY NO. 699

Toluene--Static Fire

Description: Static sparks caused a solvent fire with an unusual sequence of events. While toluene was being transferred by a hand pump from a drum to an ungrounded pail, a static spark jumped from the nozzle to the pail, igniting the toluene. The nozzle was dropped and toluene syphoned from the drum to the floor of the main work area. This pump was the only one of 14 in the plant that did not have a syphon breaker.

While employees attacked the fire with extinguishers, the fire door in the opening to an adjacent flammable liquid mixing room was closed, but due to the absence of a curb, burning liquid flowed under the door. After the fire in the main work area was put out with extinguishers, the door to the mixing room was momentarily opened. Flames burst out and reignited spilled toluene. Fire in the main work area was put out for the second and last time by 12 sprinklers and a carbon dioxide hand hose line. The fire in the mixing room was extinguished by a carbon dioxide flooding system and three sprinklers.

CASE HISTORY NO. 700

Polyethylene Liner--Static Fire

Description: Static fire from a polyethylene liner at a production plant caused essentially no damage. The operation involved charging the chlorothiazide intermediate we call DSA (Chlorodisulfanyl aniline) to tetrahydrofuran in an agitated still. The dry DSA is scooped via a stainless steel scoop from a polyethylene lined fiber drum into the vessel through a 13 x 15-inch manhole. A slight vacuum is maintained in the vessel to minimize escape of fumes and dust.

On this day, one drum was scooped into the vessel and when the drum was nearly empty he removed the liner from the drum and shook the remainder into the vessel. When the operator shook the second bag over the manhole, a sudden flash occurred and flame billowed out of the manhole. The man's hair was singed but he and two others extinguished the flames quickly with extinguishers before sprinklers operated. Relative humidity was found to be 50%.

Preventive Measures: This incident reaffirms the need for strict adherence to the policy of not shaking plastic liners over manholes. Ventilation of vessel manholes should be provided outside the manhole. Vacuum should not be cracked into the vessel since it sweeps in sufficient air to give a flammable mixture. Whereever possible, we should eliminate the use of polyethylene liners in flammable areas.

CASE HISTORY NO. 701

"Boil Over"--Flash Fire

Description: Early on the shift, the shift leader had charged nitrocresol into an autoclave as the first step in making a batch of nitrocresol methyl ether. Later when the operator went to the floor below to shut off the flow of methyl alcohol, the special operators, acting as helpers, dumped flake caustic into the autoclave. When the operator returned, and without checking the agitator he had the two help him add soda ash. He did not recognize the hazardous situation at the blender from the presence of a caustic and a nitro body in an unagitated vessel. When a third bag of soda ash was added, the charge erupted through the manhole with force sufficient to reach the roof, splashing all three men with the material. A flash fire followed. The clothing of the helper who was directly in front of the autoclave was soaked with the flammable mixture which ignited while he was in flight from the area even though it had been flame-retardant treated.

Cause: Incident was caused primarily by the failure to start the agitator in the kettle and, secondarily, by the improper sequence of charging materials, both being deviations from the printed operating procedure.

Preventive Measures: Supervision and operators are being reinstructed on the necessity of following operating instructions at all times. In addition, consideration is being given to the probable value of installing a visual alarm system on critical vessels to show the status of agitation.

CASE HISTORY NO. 702

Fatal Injury--Tube Carrier

Description: Tube carriers are used at this plant to convey orders and small test samples. These carriers are the familiar "Lamson" tubes frequently seen in department stores to carry slips and change. Some tubes used by this plant are larger than the department store variety. This particular system was manufactured by the Grover Company.

Cause: This accident occurred on a four-inch tube system when a carrier became stuck between buildings.

To free the carrier, mechanics separated the line and pulled one section to one side. As it tended to spring back into line, a screwdriver was jammed between two of the tubes. Compressed air was applied to the end of the tube. The injured man, standing on a ladder and not in direct line, was apparently struck by the emerging carrier which was deflected enough by the screwdriver. He fell backward, approximately eight feet, to the concrete floor, the back of his head striking the floor.

Preventive Measures: It is not generally good practice to use compressed air to free stuck carriers but if this has to be done, arrangements should be set up to catch a carrier or otherwise make sure that everyone is safely out of the way. A truck size innertube has been used successfully to catch the carrier.

CASE HISTORY NO. 703

Explosion in Vent Stack- Static Generation

Description: An employee was repairing a blower on an exhaust vent system for a 1200 gallon dissolver. After lubricating the fan shaft of the blower, he turned on the switch. As he returned to the vent stack, he observed that the blower was not operating. When he leaned over the open vent stack and reached down into the stack to give the fan a turn, a flash fire and explosion occurred. The employee received moderate to severe burns to the head, face and hand.

Cause:

1. The employee was wearing street clothing, underneath coveralls of synthetic fibers which probably built up a static electrical charge. The electricity probably discharged when the employee reached into the vent stack.
2. The vent stack contained an explosive mixture of methyl alcohol and benzene.

Preventive Measures:

1. Use of an inert gas blanket on the dissolver when maintenance work is being performed.
2. Study the process to eliminate the oxygen from the system.
3. Reinstruct all employees on the potential hazards of static electricity relative to types of clothing, static potential of workmen, etc.
4. Emphasize to all employees the hazards of reaching into electrically energized equipment.

CASE HISTORY NO. 704

Machine Operated with Guards Removed

Description: New molds had been placed in a high speed, fully automatic plastic injection molding machine. The machine is equipped with both hydraulic and electrical interlocks for accident prevention at normal operating sites. However, only the operator's gate with interlock had been put back on the machine and the back part of the guard which is usually fixed in position was left off. During a trial run, an operator reached into the mold in an attempt to make adjustment of a platen from this unguarded back side of the machine when his hand was caught.

Multiple fractures and severe contusions of left second, third, fourth, fifth fingers. Eventual amputation of major portions of third and fourth fingers.

Cause: Unsafe Condition

Incomplete Design - The machine is well engineered from a safety standpoint except for the lack of interlocks for the back guard.

Unsafe Acts

Removing Safety Devices - It is necessary to remove the back guard to change molds; however, the guard was not replaced at completion of installation of the mold.

Failure to secure equipment while making adjustments. - Adjusting moving equipment.

Preventive Measures: Immediate

1. Extend the interlock system to include the back guard.

2. Incorporate safety in the operational instructions emphasizing that moving equipment must be secure before making adjustments.

3. Continue the emphasis on safety awareness through the formalized monthly safety meetings.

Long Range
The feasibility of extending the lockout procedure to cover the routine operating equipment should be considered.

CASE HISTORY NO. 705

Kettle Over Pressurized--Near Miss

Description: At 3:45 p.m., February 28, 1961, approximately one-half batch (13,000 lbs.) of Lytron 215-S was vented through the rupture disc of the latex kettle to the roof and surrounding areas.

There were no injuries or equipment damaged.

Lytron 215-S, batch 2325, was processing normally in the 3700 gallon Pfaudler kettle. The operator applied nitrogen to the kettle to suppress foaming per standard operating procedure. After opening the nitrogen inlet valve, he left the kettle to prepare raw materials for further processing. Approximately 5 minutes later, the department foreman hurried into the area and informed the operator that the batch was spewing onto the roof. The operator became aware that he still had nitrogen pressure on the kettle and had not checked it recently. He immediately shut off the nitrogen inlet valve and flash cooled the batch.

Subsequent investigation by the committee showed the rupture disc had burst due to excessive (approximately 35-40 psig) pressure and safely vented the material to the roof.

Cause: Investigation of the equipment, process records, and interview with the operator indicated that the processing of the batch was normal. However, the mechanical arrangement of nitrogen connection to the kettle and the standard operating procedure of applying nitrogen allowed inadvertent overpressurizing of the kettle. The present nitrogen system will deliver a maximum of 50 psig of pressure to the kettle while the rupture disc will burst at approximately 28 psig at 212°F.

Preventive Measures:

1. Provide positive pressure control (20-25 psig) on nitrogen charge line.

2. Provide spring-loaded control on the present nitrogen inlet valve until the first recommendation is completed.

3. Investigate the need for similar protection for the air line connected to the kettle.

4. Due to other possibilities of overpressurizing the kettle; e.g., bringing a batch into reflux with the vent closed, it is recommended that a pressure sensing and warning device be installed on the kettle.

CASE HISTORY NO. 706

Dust Inhalation--Formaldehyde Derivative

Description: The employee was loading a 300 gallon kettle with sixteen bags of a formaldehyde derivative. After emptying each bag into a funnel equipped with a ventilating hood, he piled the empty bags on the floor behind him. After he had emptied eight bags, he compressed the pile of bags with his hands, causing a dust cloud. The man breathed some of the dust which resulted in an asthmatic response. (One week before, this same employee had received a gross exposure to an organic vapor which may have caused sensitization to the formaldehyde derivative.)

Cause:

1. The emptied bags contained a residual amount of the formaldehyde derivative.

2. The bags were piled and collapsed on the floor instead of in the hood provided.

3. Although the employee knew the toxic properties of the material, he did not realize the danger of a limited exposure to the organic dust.

Preventive Measures:

1. An environmental survey of all the production area will be made to determine the exposure level of employees to hazardous materials.

2. All employees will be reinstructed on:

   a) The hazardous properties of chemicals in the process.
   b) The proper job procedures, including use of personal protective equipment, to protect themselves from exposure.

CASE HISTORY NO. 707

Chlorine Released Unexpectedly

Description: Five pipefitters, working at two locations on the high pressure chlorine line, inhaled chlorine vapors flowing from the open line. The fitters were treated at the dispensary and released.

The high pressure chlorine header was being modified as part of the VCM expansion program. The line on which the fitters were working was to be raised and had been cut on two sides. A connecting line leads to the tank car rack, and is used to pressure tank cars for unloading them into chlorine storage tanks.

This high pressure header and all branches from it were thoroughly purged with nitrogen except the connection to the car rack which had been overlooked. The supervisor recognized that the line had not been purged, but had assumed that the Valve "A" next to the tee was closed. While the job was in progress, he decided to check the valve next to the rack to make sure it was free of chlorine before this line was cut so that the header could be raised. The unpurged line was connected to four unloading spots at the car rack. At two of these spots, there are valves which were closed and not connected to other piping. On the other two spots, similar valves were also closed, but were connected to a piece of hose on the end of which was a valve and each of these hose connections was equipped with a bleeder and pressure gauge. Prior to the accident, all of these valves were closed. The production supervisor observed no pressure reading on Gauge "D", and erroneously assumed no chlorine had been trapped between "A" and "B". He did not observe "G". He therefore directed Valve "B" to be opened prior to Valve "C" as he anticipated opening Valve "C" last to check for chlorine. The car loader observed a 25 psig reading on Gauge "G"; without questioning the action, he opened Valve "B" as he had been requested. The hose was apparently partially full of liquid chlorine which depressured through Valve "A" (later found to be frozen in a partially opened position) into the high pressure chlorine line on which the fitters were working.

The fitters were in weather and spark enclosures in the pipe rack which made their escape from chlorine more difficult. It was fortunate that they were not injured more severely.

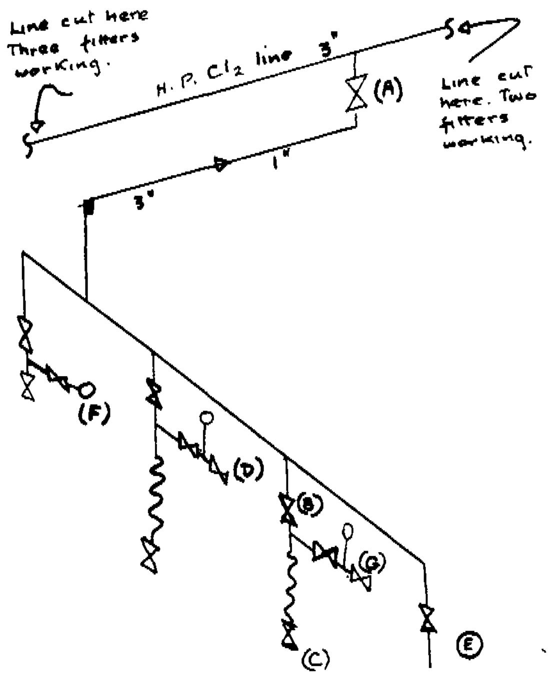
Cause:

1. The lines were not properly prepared for maintenance by the operating personnel who purged the system.

2. The checks by the production supervisors and chief operator were not sufficiently thorough before signing the permit for work.

3. The work was not stopped when it was discovered that the basis for which the permit was signed (a decontaminated system) was not valid.

4. Improper communication between production and car loading personnel.



5. Failure to question the opening of a valve when pressure indicated that chlorine was trapped in the hose.

6. The production chief operator was not aware that an attempt was being made to check the loading line for chlorine.

Preventive Measures:

Production

1. The facts in this case were reviewed with the fitters involved to assure them of the company's concern, and of the follow-up action to be taken.

2. Appropriate facts of the case were reviewed in detail with VCM operating personnel.

Maintenance

1. A review will be made of the possible safety hazards connected with the use of weather and spark protection enclosures in pipe racks.

2. This incident will be studied as to the advisability of additional protective equipment for work of this type.

Material Handling

1. This incident was reviewed in detail with the car loaders and their supervision.

CASE HISTORY NO. 708

Steam Hose Frozen--
Employee Burned by Steam

Description: A tank farm helper had cracked the valve, allowing steam to pass into a 14-foot length of one-inch steam hose that was frozen to the ground. The hose gradually thawed out except for a short section near the nozzle end. To expedite the thawing, he exposed this frozen end under steam from another line, holding the hose two to three feet from the nozzle. Although the valve to the hose was only cracked, it can be assumed that the pressure in the hose built up to line pressure of 120 pounds. This caused the front section to whip around when it thawed out, scalding the front of the helper's neck. He threw the hose away from him and immediately reported to the plant dispensary for treatment.

The injured was wearing goggles, gloves, rubber footwear, hat and heavy winter clothing at the time of the incident.

The investigating committee, in checking the area, noted that there was no hose rack available. Consequently, the hose was laid on the ground when not in use. This resulted in the hose freezing to the ground, and the condensate freezing in the hose.

Cause:

1. No means available for supporting hose off the ground.
2. No provision made to drain condensate when steam is turned off.
3. Improper method used by employee in holding hose.

Preventive Measures:

1. Install hose rack to support hose off ground. Rack should be constructed at an angle to allow hose to drain.
2. Instruct Tank Farm personnel on proper handling of hoses under pressure.

CASE HISTORY NO. 709

Anhydrous Ammonia Burns Are Painful

Description: Liquid ammonia splashed on back of employee's hand as he lifted carrier containing two liter flasks to place it in the fume hood. Flasks were closed with rubber stoppers having 9/16-inch holes in center and were sitting upright in carrier. The stopper of one flask blew out and splashed liquid ammonia upward and onto hand of employee. The flask was not broken.

Cause: When dry, pure liquid ammonia is allowed to stand for a time at room temperature in an extremely clean flask, boiling is slow to start which results in a build-up of heat in the liquid. A small bump or jolt will start the liquid boiling. If the liquid has accumulated enough heat before the boiling begins, the beginning can be one of considerable force—enough to blow the stopper from the flask along with a large part of the liquid.

Preventive Measures: Instruct employees to: use rubber gloves; wear goggles; be careful when approaching or lifting a quiet or non-boiling flask of liquid ammonia; be careful not to bump into another person or object when carrying liquid ammonia; always place five or six grains of oil-free sand in bottom of each flask before filling, this will aid boiling and prevent build-up of heat.

CASE HISTORY NO. 710

Valve Failure--Caustic Injury

Description: A fusion reactor operator opened a 1/4-inch valve in the steam-out line to the "east fusion reactor 70 per cent caustic rotameter." Steam and caustic immediately sprayed out of the valve stem packing, striking the operator on the head and shoulder area. A first degree burn on the left eyelid resulted. Further eye damage was prevented by the safety glasses worn by the injured operator.

The operator flushed his eye with water. Subsequent medical care was received at the hospital.

Cause:

1. The 1/4-inch gate valve packing nut became loose, allowing the packing to blow out when the valve was opened.
2. The 1/4-inch stainless check valve between the rotameter and steam valve leaked, allowing caustic to be present in the steam.

Preventive Measures:

1. Maintenance supervision to emphasize the need for properly adjusted valve packing upon installation.
2. Production supervision to emphasize the need for maintaining proper valve packing adjustments. (Wrench tightened to allow no product leakage but free valve stem movement.)
3. Engineering study to be made by a representative of maintenance and Technical Service Department to design an effective system for the inter-connection of chemical and utility lines which will prevent chemical contamination of steam and water

supplies. Recommendations to be specific for the fusion caustic rotameters but applicable in similar situations throughout the plant.

4. Supervision of all departments will emphasize the need for eye protection using the background information from this investigation. Briefly, this information is:

   a. From his experience, the injured operator feels that eye damage would have been more extensive if safety glasses had not been worn.

   b. This was a clear case of the unexpected eye hazard. The fact that many eye injuries can be prevented or minimized by the use of safety glasses is borne out by this example.

   c. Although not normally used in this operation involving closed piping, goggles would have completely prevented eye injury. This illustrates the need for the greater protection offered by goggles and face shields where known hazards exist or the hazard exposure is uncertain.

CASE HISTORY NO. 711

Unlabeled Bottles Are Dangerous

Description: An instrument man was slightly burned and his clothing partially destroyed when an unknown chemical erupted from a sink drain in the analyzer shop. The instrument man was preparing "printed circuit" board. This board is a Micarta sheet with a thin copper sheet pressed to the Micarta. Tape is placed on the copper sheet, following the desired conductor paths. The board is then dipped in a ferric chloride solution which dissolves the exposed copper. The board is then rinsed with water.

The instrument man selected an unlabeled one-gallon bottle from the chemical supply cabinet. Although the color of the contents looked like ferric chloride, he asked the supervisor standing nearby if the bottle contained ferric chloride. The supervisor said that he did not know. The instrument man then poured some of the liquid from the bottle and used it in an effort to prepare the board, but nothing happened. He then discarded the liquid by pouring it into the sink drain, and as he was reaching for the water faucet to turn it on, the sink drain erupted. In subsequent investigation, none of the supervisors or instrument men could remember what this chemical was or why it was brought to the shop.

Cause: The primary cause of the accident was the unlabeled material in the chemical supply cabinet.

Also, a lack of safety consciousness on the part of the individual concerned was evident. The instrument man did not know the contents of the bottle—he knew he did not know. He made a tentative attempt to find out what the material was, but did not follow through and subsequently handled the material without the proper respect for the unknown chemical. The supervisor who was asked to identify the material, even though he, himself, did not know, did not follow through to see that the proper chemical was found and used.

Preventive Measures:

1. All bottles of needed chemicals stored within the instrument department have been properly labeled with suitable handling precautions listed.

   All unidentified and unneeded chemicals have been disposed of, and this incident has been thoroughly discussed with all instrument personnel.

2. Because the potential exists, plant-wide, for a similar accident to occur, all departments have been asked to survey their chemical storage cabinets of bottles and other similar containers, dispose of those not identified, or not needed, and properly label those needed chemicals within their departments.

CASE HISTORY NO. 712

Ethylene-Air Mixture in Pipe Exploded

Description: Two pipefitters were engaged in running a 1-inch pipeline from the ethylene surge tank to the ethylene distribution header. This job was being done prior to a scheduled shutdown so that the ethylene system could be depressured and the ethylene recovered. The line from the ethylene header was started by connecting into two 1/2-inch connections on the ethylene header and laying 75 feet of 1-inch pipe along the south wall of the compressor house. After this temporary line was completed up to the surge tank, a closed valve was installed on the end of the new line. Later, it was decided by the pipefitters that a union should be installed ahead of the valve, and so they proceeded to remove the closed valve. As this valve was unscrewed from the pipe, and at the moment it cleared the last few threads, a small explosion occurred—the gas from the pipe ignited. Both the pipefitters were singed about the head. A fire extinguisher was used by an operator to put out the fire.

Cause: Probably ethylene pressure built up within the 1-inch line against the closed valve as a result of a leak through the ethylene header connections. It is believed that the mixture of air and ethylene in the line was ignited by a frictional spark resulting from the unscrewing of the valve from the pipe.

Preventive Measures:

1. All maintenance personnel would be informed not to remove a closed valve from a line once it has been tied in to a process source without first depressuring the line safely.

2. Production also consider all valve connections into process as potential leakers, and provide a bleed valve on the open end on a new line until that line can be finally tied in. Wherever possible, all tie-ins to valves that are connected to processes will be made last.

3. In other situations similar to this, production will have pipe connections checked for possible leaks prior to tieing in, and maintenance personnel will be informed if "operations" is unable to stop the leak.

CASE HISTORY NO. 713

Operator Sprayed When Blocked Line Opens Up

Description: In the early stage of transferring a batch of isopropyl 2, 4-D ester, from the reactor to a receiver, the discharge nozzle of the vessel became blocked. An operator, who was on the second level at that time, attempted to unblock the discharge nozzle with a metal rod through the opened manhole. He was not successful. Another operator tried to blow back into the bottom of the vessel by applying nitrogen gas pressure to the transfer line at ground level. However, the pressure on the nitrogen cylinder was too low to be effective. The chief operator was called for assistance. He had a new cylinder of nitrogen installed by a night mechanic. In the meantime, the operator upstairs was still trying to unblock the nozzle via the open manhole. After the new cylinder was installed, the chief operator applied pressure on the transfer line in an effort to unblock the line at the bottom of the reactor. While pressure was being applied to the transfer line at the bottom of the tank, the operator upstairs was standing at the open manhole, holding on to the metal rod which was in the discharge nozzle. He was watching to see when the blockage was opened. When he felt pressure on the rod as the blockage began to give way, he called to the operator on the ground floor level to shut the cock. Material suddenly sprayed out of the open manhole and dropped down on the ground level operator.

He was assisted to the safety shower where he was washed and his clothes were removed. He was then taken to the dispensary for treatment.

Cause: In the manufacture of isopropyl 2, 4-D ester, considerable quantities of small "balls" of apparently unreacted 2, 4-D acid and/or sodium salt of 2, 4-D acid are formed. These so-called "balls" frequently plug up the discharge nozzle of the reactor. When blockages occur, an attempt to clear the nozzle is made by pushing a steel rod through the open manhole into the nozzle. When this does not work, an attempt is made to unblock the line from the discharge side of the nozzle. If blockage is between the nozzle and pumps, rod-out ports are available to clear the horizontal section of the line. Space does not allow a conventional rod-out to be used to clear the vertical section leading to the bottom nozzle. In order to clean out this section, nitrogen gas pressure is applied to the transfer line so as to blow back into the vessel. When gas pressure is being applied, the man stationed upstairs watches for bubbles as evidence of blockage being broken. This method was being followed when the accident occurred.

The Committee feels that the prime factor contributing to the accident was the open manhole while pressure was being applied on the discharge side of the tank. Had the manhole been closed and secured, the Committee believes that the accident would not have occurred.

In the course of the investigation, the regulating valve on the nitrogen cylinder was examined. The valve was found to be operable. However, process material was found in the regulator. This valve was not installed according to Procedure 362 which calls for a bleed valve and catch pot to be installed on the down stream side of the regulator.

Preventive Measures: Departmental

1. Install a flush bottom valve on the bottom of the vessel to eliminate the need for rodding-out discharge nozzle.

2. Investigate a method of charging 2, 4-D acid into the reactor to determine if "balling" of unreacted 2, 4-D acid and/or sodium salt of 2, 4-D acid can be minimized. Also, obtain a sample of the "balls" and determine the composition by laboratory analysis.

3. Technical Service Department is to design and have installed an improved mechanism for holding back the charge of 2, 4-D acid in the charging hopper.

4. Maintenance Department is to provide a plate floor around the front portion of the reactor.

5. In the event that Item 1 proves to be unsatisfactory, Technical Service Department is to design and have installed a

permanent rod-out mechanism for the bottom nozzle of the tank. The effectiveness of Item 1 must be determined within 30 days after the start of 2, 4-D ester production run. If rod-out is needed then, it should be installed within one week after Item 1 has proven unsatisfactory.

6. Should neither Item 1 nor 4 prove satisfactory, then a dip pipe for transferring the batch is to be installed. This method should eliminate any need for blowing out the transfer line.

General

1. Manhole covers should be closed and secured while introducing any form of pressure into process vessels. Immediate adoption of this practice is required.

2. Goggles are to be worn when looking into open manhole of process vessel. Production Department is to incorporate this practice in their operating instructions where applicable. Also, this practice is to be discussed in the next regular departmental safety meeting.

3. Production supervision is to survey all regulating valves on pressure systems in their departments to determine if these valves have been installed according to Procedure 362.

4. Maintenance Department is to issue a revision to Procedure 372 which will include a pop-off valve between catch pot and reducing valve.

5. Standard written instructions for the operation of pressure control systems are to be posted near the operation.

6. Special operating training instructions for the people concerned with operating these pressure systems are to be given by Production Department supervision.

7. Departments using pressure systems are to include these systems as items to be checked on their regular monthly safety inspection report.

CASE HISTORY NO. 714

Explosion Involving Tollen's Reagent

Description: After following the course of a reaction by periodic testing of samples from the mixture of Tollen's reagent, a research chemist allowed the unemptied test tubes from the testing to sit over the weekend. Monday morning, upon picking up the test tubes to dispose of the contents, an explosion occurred, splattering the contents into the face and on the upper body of the chemist, and onto the laboratory ceiling. Fortunately, the chemist was wearing safety glasses. No serious injury resulted.

Cause: The docket of cases involving violent explosions incurred while working with ammoniacal silver ion solutions is a very long one. In using such solutions, it is difficult not to form fulminating silver. Although the exact structure of the latter is not yet known, it is thought to be either Ag_3N or Ag_2NH. Dry fulminating silver is extremely sensitive and is instantly and violently decomposed by the slightest disturbance. Even still moist fulminating silver can be detonated by allowing a drop of water to fall on it from a sufficient height.

Preventive Measures: Consequently, great care should be taken in the preparation and use of Tollen's or similar ammoniacal silver reagents. The procedure given in Vogel's "Elementary Practical Organic Chemistry", Vol. II, p. 406, is recommended. The reagent must not be heated. It should not be prepared in large amounts and stored; only a small volume should be made up just before use. Any residue (both before and after use) should be washed down the sink immediately with copious amounts of water and the container rinsed with dilute nitric acid. Above all, do not allow the reagent solution or any test mixture containing the reagent to evaporate to dryness.

CASE HISTORY NO. 715

Overhead Guard on Fork Lift Truck Saves Operator

A load of paper pulp, weighing about one ton, fell on top of a fork lift truck guard. The shock bent the frame slightly as illustrated in the photograph (next page). The operator was fully protected and therefore was not injured. The top of the pile extended about 12 feet above the truck so the average drop of the paper was about 8 feet before striking the guard. Structural engineers say that this is somewhat equivalent to dropping 8 tons from a height of one foot on top of the guard.

Years ago, when fork lift trucks were introduced, the need for overhead protection was recognized. Standards for guards were developed through design and tests. The adequacy of these guards has been demonstrated on several occasions. Each time the guard prevented injury. The operator's first reaction is to escape, to avoid by jumping or running away. This urge was fortunately curbed by the operator and he stayed in the safe cage made by the guard and the truck.

Safety know-how coupled with engineering design in preplanning of any condition or machine always spells "Safety Pays".

CASE HISTORY NO. 716

Fork Lift Accident with Drum

Description: The drum containing trichloethylene and weighing 7 cwts. was being up-ended with the aid of the pedestrian operated fork lift.

The fork lift operator was manually assisting in the lift when the drum slipped and the injured's hand was caught between the chime of the drum and the forks of the fork lift.

The drum was being up-ended to enable a small bung on the end to be removed and replaced by a tap. If the drum is not up-ended, the ullage is such that spillage occurs when the bung is removed. The ullage of the drum measured through the empty bung was 2-1/4 inches.

Cause: The Committee, after reading the statements of witnesses and the shift foreman, visited the scene of the accident and inspected the fork lift and a similar drum to the one that caused the accident and carried out similar operations to the one during which the accident occurred. It was observed that the drum was of the hooped type. When the drum was lifted with the aid of the fork lift after the forks had been inserted up to, but not beyond the first hoop, it was seen that a stable lift was never possible and the drum always fell back to the floor. With the forks inserted beyond the first hoop, the drum was easily lifted to the vertical position without any assistance being given, other than the lifting action of the fork.

The Committee later watched an operator demonstrate the removal of a drum from the top level of the drum storage rack, lowering this to the ground floor, up-ending and then replacing the drum in the rack in the horizontal position.

As witnessed by the Committee, there was no indication that the normal operations carried out with this fork lift were in any way unsafe. As demonstrated, it was quite safe to up-end the drum, providing the proper method was used. It was felt that it was not really necessary to have up-ended the actual drum which caused the accident, since one end of this drum could have been rolled up on to a special type of wedge known as a fish, elevating one end only. The bung could have been safely removed without spillage of the contents.

All the operators engaged on fork life work at this location have received instruction in the use of this machine; but in the opinion of the Committee, the standard of proficiency and the amount of practice which the individuals have had, varies considerably. No written instructions are issued to fork lift drivers, although instructions are available including a list of "Do's" and "Don'ts."

The fork lift involved in the accident is unique on the site, since it is power lifted and pedestrian propelled. Because of this, there were hazards associated with this machine which would not apply to all other fork lifts used on the site.

Preventive Measures:

1. A basic course of instructions should be defined and all operators given a set of instructions after training.

2. Only operators specifically nominated by Shift Foremen and upwards will operate the fork lift.

3. The present verbal instructions to operators assisting fork lift drivers not to assist in handling the load in any way while the forks are lifted off the ground, should become part of the written instructions and strongly emphasized. This recommendation would apply to all fork lifts on site.

4. All personnel trained in fork lift work should be contacted and the fact emphasized that when using this particular machine, the forks must be inserted past the first hoop when a drum is being up-ended for a safe lift to be accomplished.

5. For removing bungs and inserting taps in full drums, the use of a fish, i.e., a short wooden ramp, should be tried out. This would enable the drums to be tilted sufficiently to prevent spillage when the bung is removed and would avoid the difficult manual operation of tipping it back on its side.

CASE HISTORY NO. 717

Propellant Explosion

Description: An employee was working with an experimental mixture for a propellant in a dry box (controlled argon atmosphere cabinet). While working in the dry box, he had completed mixing two chemicals in a polyethylene beaker and set the beaker to one side. He thought he noticed a discoloration taking place in the beaker. He tilted the beaker with his left hand, and an explosion occurred. The safety glass front of the box was blown out. The employee received a severely lacerated left hand with loss of the tip of the little finger. He also sustained moderate cuts about the face.

Cause: The exact cause for the explosion is not known.

1. The employee was working with experimental propellants which entails the use of many kinds of high energy chemicals.

2. The employee mixed too much of the material in the dry box at one time.

3. The employee handled the beaker when discoloration had occurred.

4. Improperly designed equipment.

Preventive Measures:

1. More careful control of chemicals being worked with or stored in the dry boxes is to be reemphasized with all employees.

2. Reinstruction to all employees on keeping experimental mixtures to a minimum size and the use of tongs and shielding whenever possible for manipulating materials and equipment.

3. The feasibility of remote tongs being used through a ball joint is being considered.

4. A dry box is being investigated which will relieve pressure through the back in case of an explosion.

CASE HISTORY NO. 718

Thermal and Chemical Burns to Both Eyes

Description: On the day of the accident the injured was performing the normal duties of the extra-day operator in the phthalic anhydride refinery. These duties include, among other housekeeping jobs, cleaning any material build-up from around the packing glands of the column feed and reflux pumps.

During the course of cleaning the #2 reflux pump, the injured reports that his goggles became fogged and as he stepped back and removed them he was sprayed with molten phthalic anhydride from the pump. The respirator he was wearing protected the lower part of his face; however, the material sprayed into both eyes. His calls for help were apparently unheard and he immediately proceeded to the dispensary unassisted. Shortly after reaching the dispensary and during attempted treatment for the eye injury, he collapsed from a severe attack of asthma. Simultaneous artificial respiration and deep heart massage were used to revive him and after treatment for the eye injury and oxygen treatment he was removed to the hospital.

The quick action of the dispensary personnel unquestionably saved his life and the Committee highly commends the dispensary staff for their prompt and efficient actions.

Cause: There are six horizontal centrifugal pumps in the distillation and stripping section of the refinery (four normally operating and two spares) that require cleaning due to leakage through the packing. The normal cleaning operation is to use a flat-bladed chipping bar to remove the build-up of crystallized material while the pump is operating. An examination of the pump and operating data indicated no unusual or abnormal conditions at the time of the accident. It is not unusual to find a pool of liquid material at the center of the incrustation; however, the spray-out that resulted in this accident is not normally encountered. There is no logical explanation to account for the spray in this instance, and not in other cases, except a possible variation in cleaning technique. It is the opinion of the Committee that the spray resulted from the rotating shaft and that a hazard exists with any cleaning technique while the pump is running.

Preventive Measures: Immediately after the accident, the department supervisor made an investigation and advised the Committee of his immediate actions.

1. Use of goggles, face shield, apron and gloves shall be mandatory while working on all pumps.

2. New thermometers will be installed on all jacketed packing glands to assist in maintaining proper cooling water temperatures.

3. The use of a shield over the packing gland of all pumps in the distillation and stripping section to be considered. This recommendation is made to eliminate the possibility of the pump spraying the area during normal operation.

In addition to these items, the Committee makes the following specific recommendations:

A. Insofar as possible, no attempt at cleaning should be made with the pump operating. (Sufficient spares are available on the column pumps to make this practical and the stripping still pump can be shut down for short periods for cleaning without affecting operation of the still.)

B. As part of the recommendation regarding personal protection, signs should be installed in the area of the column pumps as a reminder to employees to wear proper protection.

C. The possibility of replacing the packing glands with mechanical seals should be investigated by the Maintenance Staff Department.

It is further recommended that all department supervisors review their departments to determine the extent of any similar hazards and take any or all of the above recommendations as required.

CASE HISTORY NO. 719

Peroxides Again (See Case History No. 603)

Description: A bottle of urea peroxide erupted, showering the laboratory with urea peroxide. This incident occurred because the urea peroxide had been standing in a closed cabinet together with inorganic chemicals for approximately four (4) years. The urea peroxide was in a wide-mouth, 4-liter brown bottle with a plastic cap.

Cause: It is surmised that the urea peroxide started to decompose, releasing sufficient oxygen to shatter the cap and to push open the cabinet doors. The peroxide was thrown around the laboratory from the sudden release of pressure. While no one was injured in this situation, it again points out the need for maintaining accurate inventories. It also calls attention to the necessity for close checks on the storage of peroxide materials and other unstable chemicals.

Preventive Measures:

1. Supplies of peroxide materials should be kept at a minimum and stored for no longer than six months.
2. They should be stored in cool places.
3. They should be stored away from organic materials.

CASE HISTORY NO. 720

Explosion in Oxygen-Nitrogen Manifold

Description: An explosion occurred in the oxygen-nitrogen manifold which feeds an experimental unit. The laboratory technician opening the oxygen valve received lacerations to his left hand when the explosion ruptured a stainless steel tee.

The experimental unit was being started up by normal procedures during which a nitrogen purge was required to be followed by oxygen introduced through a manifold into a hydrocarbon stream. However, there was a delay involved and a nitrogen purge was used for some 3-1/2 hours before the unit was ready for oxygen addition. As soon as the oxygen was introduced, the explosion occurred.

Cause: Sometime during the 3-1/2 hour period in which the nitrogen purge was used, the hydrocarbon process pressure must have exceeded the nitrogen cylinder pressure, allowing hydrocarbon to flow back through the manifold and into the nitrogen bottle. This is substantiated by a subsequent analysis of the contents of the nitrogen cylinder which showed a 2 mole % of hydrocarbon in the nitrogen. When oxygen was then introduced, it is assumed that this line was still contaminated with hydrocarbon which exploded.

Preventive Measures:

1. The complete system, including the nitrogen-oxygen manifold, will be enclosed within a steel barricade, and all block valves will be replaced by remote operators.
2. Extensive revision will be made to the instrumentation and control system so that flow reversals or other upsets will automatically shut down the system.

CASE HISTORY NO. 721

Handling Sensitive Explosive Material

Description: A research chemist was uncertain as to the present purity of a substance prepared eight months earlier and attempted to recover what material he could from the sample. He placed the sample in a solvent and started to filter the solution using a sintered glass filter and a vacuum filter flask. As the filtration was in progress, the material exploded. The employee received puncture wounds and lacerations of hands and puncture wounds to his cheek and chest from the flying glass.

Cause: The chemical which exploded is relatively safe to handle when damp, but is shock sensitive when dry. It is believed that a portion of the material became completely dry on the filter and detonated when the employee touched it.

Preventive Measures: Future operations of this nature will be performed in a laboratory hood with additional personal protective equipment provided the employee.

CASE HISTORY NO. 722

Bright Sunlight Increases Eye Hazard When Arc Welding

Description: A boiler maker was working in an area with four welders. The job consisted of welding sections of a tank together outdoors. During the welding time, 4 to 5 hours, the boiler maker received an ultra violet exposure to his eyes from the arcing of the electrode. Employee received moderate to severe welding flash burns to both eyes.

Cause:

1. The arcing of the electrode gives off ultra violet rays.
2. The employee observed the welding arc on occasion.
3. The sun was bright, making the arcing less noticeable. (Arcing inside a building gives more warning from the brightness and reflection.)

Preventive Measures:

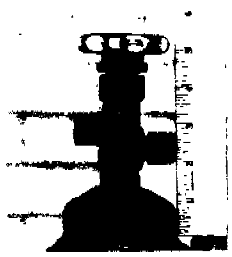
1. The boiler makers and helpers working directly with welders will be instructed to avoid welding flashes to their eyes by:
   (a) Wearing adequate eye protection.
   (b) Avoiding exposing the eyes to the welding arc at all times.
   (c) Being aware of the increased hazards from radiation in bright sunlight.
2. Employees, who are not directly connected with arc welding operations, will take necessary precautions to shield their eyes from arc producing equipment.
3. In order to help insure the safety of others, the welder should provide a "screening shield" around his work area whenever possible.

CASE HISTORY NO. 723

Hydrogen Hazard

Description: An accidental release of hydrogen from a compressed gas cylinder necessitated an emergency evacuation of personnel from a process laboratory. The incident occurred shortly after a full cylinder of hydrogen had been delivered to the chemical laboratory. The main cylinder valve was unavoidably opened as the protective cap was unscrewed from the cylinder. Because of the sudden and uncontrolled release of hydrogen, the occupants immediately left their laboratory and warned personnel in adjacent laboratories to leave the building.

Cause: When the protective cap was screwed down on the cylinder, the interior of the cap probably contacted the valve handwheel. As the cap was unscrewed, the handwheel was turned simultaneously, opening the valve and permitting hydrogen to escape.



As indicated in the photographs, the distance from the threaded portion of the dome to the top of the handwheel varies. Maximum clearance between the valve handwheel and the interior of the cap is dependent upon complete insertion of the valve into the cylinder dome. A second important variable is the number of threads present on the cylinder dome.

Preventive Measures: Suppliers of our compressed gas cylinders have been informed of these details and asked to remedy this problem. As an additional safeguard, our stockroom personnel will loosen and then gently retighten caps on all cylinders before they are put in use. A similar practice will be followed before compressed gas cylinders are taken into process laboratories.

CASE HISTORY NO. 724

Fatal Accident Loading Elevator

Description: An employee was using a Fork Lift Truck to load empty pallets onto a hydraulic elevator. The front part of the fork lift with the two front wheels was on the elevator car body. The elevator started to descend, pitching the fork lift forward. The employee's head was caught between a part of the fork lift and a cross beam on the hydraulic lift. The crushing injury to his head caused immediate death. Investigation revealed that the safety gate switch on the upper level was blocked out with two small pieces of wood. This would allow the elevator to be operated from the lower floor with the safety gate on the upper floor in an open position. It has been concluded that someone on the first level pushed the control button causing the elevator to descend at the exact time the front end of the lift truck entered the elevator car body.

Preventive Measures:

1. Have outside operating buttons (of constant pressure type) arranged so that lift car could only be sent from upper level to lower level by upper level control button - or lift car could be sent from lower level to upper level by the lower level control button.

2. Install additional safety switch on upper level gate in series with existing switch. Existing switch to remain in present location and additional switch to be installed in upper part of lift shaft at most inaccessible location.

3. Eliminate operating buttons inside of lift car.

CASE HISTORY NO. 725

Laboratory Explosion

Description: An employee had removed an explosive mix from a drying oven for testing. He was in the act of removing the mix from the crystal by holding the crystal in his left hand and scraping the mix with a spatula held in his right hand. The mix approximately 2.5 grams detonated. He received severe damage to his left hand including amputations to index and middle fingers, laceration and tendon damage to ring finger and fracture contusions and lacerations to little finger with minor lacerations and burns to thumb. On his right hand he received a laceration to the web of thumb and powder burns to his hand. He also received powder burns and minor lacerations to his face.

Preventive Measures:

1. In the future wet mix will be added to the ignition chamber of the calorimeter unit and then it will be dried prior to testing.

2. Employees will be instructed to refrain from holding sample mixes on watch crystals with bare hands. Forceps or tongs will be used.

3. Similar operations of this type will be conducted behind a suitable barricade.

CASE HISTORY NO. 726

Employee Fell from Top of Tank

Description: Two maintenance employees were doing repair work on a tank. One of the employees was inside the tank and the other on the outside. It was thought that all equipment was "locked out" - however a low pressure steam line was still connected. An operator turned on the steam and the steam began to escape into the tank. The man outside the tank became alarmed and hurried to aid his fellow employee in getting out of the tank. In his haste, he fell from the top of the tank resulting in an injury to his chest and lower back.

Preventive Measures: A two-way communications system between maintenance employees and the supervisor and/or operators involved, must be set up. The proper precautions must be taken to assure that employees are working safely on the equipment involved.

CASE HISTORY NO. 727

Face Sprayed with Corrosive Chemical--Loosened Sight Glass

Description: A pilot plant employee was reading a level gauge that contained corrosive chemicals. The bottom end of the tube came loose when he flicked the tube with his finger, spraying chemical into his face. The employee was wearing safety glasses but sustained eye burns.

Cause:

1. The Saran tube sight glass had been changed that morning by another operator because the old one was dirty and difficult to read.

2. The Saran tubing was connected to the gauge valve by flaring rather than with a standard gasket-type fitting normally used.

3. The equipment was operating at 13 pounds pressure.

4. Apparently the gauge tube was inadequately installed.

Preventive Measures:

1. The department has since installed regulation type gauge glass valves and is using the gasket type fitting.

2. The department is making a thorough study to determine if its eye protection standard is adequate.

CASE HISTORY NO. 728

Sprayed by Monochloroacetic Acid

Description: The monochloroacetic acid transfer pump was leaking. Two maintenance men were assigned to repack the pump and check its head gasket. Both men were familiar with monochloroacetic acid. Tank temperature of the monochloroacetic acid was 65 degrees Centigrade. A water hose was connected to be used to freeze the monochloroacetic acid in the line and in the pump. The lead man instructed the other to obtain pump packing, face shields and gloves. While he was on this errand, the lead man sprayed water on the pump. The helper returned with gloves, packing and one face shield. The packing and the face shield were placed on the pump motor and coupling guard.

The men began work, one on each side of the pump. The packing nuts were removed and the lead man removed two rings of packing. Both men hooked into and pulled the third ring. When they hooked the next ring, the rings slid out and monochloroacetic acid sprayed out of the pump. The helper ducked but the lead man received a full spray in the face.

Cause: Pressure in pump.

a. Piping expected to be pressure-venting because of weep hole in valve on recycle line to storage tank but must have been plugged since line was pressurized.

b. Failure to shut off steam (trace) left pressure on line due to heat.

c. Inadequate amount of water used to freeze monochloroacetic acid in pump. This was a judgment decision on part of man that packing would come out easier if the pump was not completely crystallized solid.

d. Lack of knowledge concerning possibility of pressure on a closed, heated piping system.

Preventive Measures:

1. Pump should be drained before packing. This applies to all pumps in the plant and prevents setting up special methods or practices for this one or any other. Review plant for pumps that must be modified and follow through to completion.

2. Treat this pump as well as all others as if it were under pressure. When "entering", use protective equipment needed to meet the inherent hazard.

3. Standard design should be used in installing sample drain and pressure indication of pump below shut-off valve and a valved drain on suction to pump.

4. Operator of department unit concerned to be responsible for making pump ready for work to include draining and be on hand until work is safely started. If department is down, the production foreman is to check unit. Operating or maintenance supervision should be notified of any unusual condition prior to commencement of work on pump or piping.

5. Mechanic to be responsible for tagout or lockout of unit to prevent operation. (Double check for remote starting location.) Also, use good judgment in challenging safe condition of the unit.

6. Install sump under this pump for draining and to wash down to sewer.

7. Insure adequate supply of protective equipment in tool room. Review availability and program with tool room attendant.

CASE HISTORY NO. 729

Finger Injury

Description: An operator sustained a major injury when the tip of his right middle finger was cut off by a rotary feed valve mechanism. Although there was no bone damage, a skin graft was necessary to properly repair the finger.

Modification to the rotary feed valve had been made on the day shift. Two holes of approximately 3/4-inch diameter were drilled in the housing of the rotary feed valve to provide venting from the star valve cavity. However, unlike other valves that had been modified, no vent pipe system was intended on this particular installation. The system of which this rotary valve was a part was returned to service at the beginning of the second shift. The operator was instructed to remove the lock and put the system into service, which he did. After making his first blend, he began transferring it through this valve to a storage hopper. Shortly after this operation had begun, he noticed a large spillage was occurring under the blender. He stopped the flow of polymer and with the rotary feed valve and blower still operating, he searched for the leak source by feeling with his hand the body of the rotary feed valve. In doing so, his finger entered one of the newly drilled holes and the vanes of the valve cut off the tip of his finger.

Cause:

1. A design change was made but not recognized as creating a hazard.

2. Communications were inadequate in that all concerned were not aware of the change

that was made and no single supervisor took prime responsibility for checking the safety of this modification.

3. The injured operator did not use a safe method for determining the source of leakage.

Preventive Measures:

1. Complete re-survey of the department's equipment for safety is to be made by production supervision.

2. Responsibilities of supervision are to be more clearly defined in the area of maintenance or modification of equipment.

3. All personnel in this department will be retrained in the specific equipment hazards of the department and of proper methods of trouble shooting.

4. Additional emphasis will be placed on communications improvement.

CASE HISTORY NO. 730

Diborane Surge Tank Explosion

Description: At 12:30 P.M. on March 15, 1961, a diborane surge tank disintegrated with severe resultant loss. The tank in question had a capacity of 2,000 cubic feet, 8 feet inside diameter x 30 feet long, and was constructed of 1-inch thick steel. It had a settling or sump tank of about 2 feet diameter of 3/4-inch thick steel. The tank served as storage for diborane and was operated between 175 and 225 psig. It was designed for a working pressure of 296 psi with a design safety factor of 4. At the time of the explosion, the pressure in the tank was 192 psig with a temperature of 12°C. From the pressure, temperature, and purity calculations, 1,775 pounds of diborane were present in the tank at the time of failure. The tank was located about 75 feet from the nearest piece of adjacent equipment and was barricaded on three sides by a 24-inch-thick reinforced concrete wall. The tank, prior to installation, had been completely radiographed and stress-relieved. The tank failure which took place fragmented the tank and made rubble out of the three barricading walls around it. Pieces of the tank traveled more than 2,200 feet. Other equipment in the area of the tank was not damaged but one piece of steel cut four process lines in a unit located 1,800 feet away. The fire which resulted from the severing of these lines was minor and completely extinguished in less than 10 minutes after occurrence.

Cause: Since there was some concern that a detonation may have occurred in the tank due to some trace impurities and in order to fully evaluate what occurred, expert consultants from outside the company were obtained. An explosion consultant examined the locale of the explosion and the debris and debris pattern and then, based on the information available to him, drew the following conclusions in his report.

"The blast pattern and magnitude of the explosion of the diborane surge tank explosion of March 15 may be explained on the basis of one of the following two mechanisms:

1. "Simple (probable defect) mechanical failure of the tank under its operating pressure.

2. "A surge of pressure, which evidently could have been produced only by an explosion of a relatively small amount of some unknown explosive condensate inside the surge tank localized at the point of initial failure of the tank."

He then continued further saying, "The writer found no evidence whatever for a contributing explosion. The evidence for this conclusion was as follows:

1. "If the surge had been uniform over the tank, bursting would have been uniform instead of asymmetric as observed.

2. "The explosion would then have been at least 7.5 times as powerful as it actually was.

3. "No apparent rocket action would then have been expected to produce the observed asymmetric damage to the barricades, the bending movement on the east concrete support, and the radially asymmetric distribution of tank debris.

4. "If there had been an initial explosion in the surge tank involving an explosive condensate, it would have occurred in the sump tank or at least on the bottom of the surge tank. No such explosion occurred since there was no localized explosion damage at these positions. Such an explosion occurring part way up the side wall of the tank would, moreover, be very difficult to explain."

Metallurgical consultants examined the physical damage to the tank. By collecting all the fragments of the tank which were available and examining these metallurgically and physically, they came to the following conclusions for the reasons listed.

"Although it was not possible to establish beyond doubt the reasons for the various failures, results of the metallurgical examination indicate the following observations:

1. "There was no evidence to prove or disprove the possibility that an external or internal explosion of small proportions may have been the motivating factor in initiating the rupture of the diborane surge tank.

2. "The combination of a serious metallurgical defect and the highly complex stress system at the attachment weld of a platform support is considered sufficiently damaging to have promoted failure by mechanical means and did not necessarily require supplementary forces that would have attended a small explosion. It is believed that the primary failure developed at, or in close proximity to, the attachment weld under circumstances normal to the prevailing operating conditions.

3. "The fracture system that originated in the area of the sump is considered of secondary significance and very probably was initiated by the explosive force that accompanied rupture of the drum.

4. "The extensive fragmentation of the drum and the brittle characteristics of the fractures were ascribable to the high notch sensitivity of the steel at the operating temperature. Improved notch toughness would have decreased the degree of fragmentation but it probably would not have prevented ultimate failure of the drum."

Based on the foregoing conclusions of these consultants plus a calculation which indicates that the same damage could have been done to the tank if only an inert gas had been in the tank, the conclusion reached is that the tank failure was precipitated by a complex stress system which had been set up by a defective welding procedure used in the installation of a platform support which had been attached directly to the tank by welding.

Comments Concerning the Explosion: On an unplanned basis, a spill test for diborane occurred. It is interesting to note that minor damage, if any, occurred as a result of the release of over 1700 pounds of diborane. Essentially, the material, as released, burned as an envelope without any evidence of detonation taking place. This is interesting since optimum mixtures of diborane in air have a flame speed of up to 2600 meters per second which is actually above detonation velocities. It is also significant that in spite of the large amount of material released and in spite of the toxicity of the material, the area was not contaminated and no personnel received over-exposures resulting in toxic symptoms and that the extent of the damage was definitely localized.

Preventive Measures: The measures taken to prevent this type of accident happening again are relatively simple.

There must be definite assurance backed up by engineering inspection that vessels which are installed in critical service do not have their properties altered by additional field welding on them unless such welding or heating is done in accordance with and to meet the conditions as originally prescribed and designed into the vessel.

A second and more important consideration involved here is to design a plant such that the inventory of hazardous material or the installation of large tanks under pressure be minimized as much as possible. In this particular case it was possible to eliminate the intermediate storage or hold-up of diborane completely by minor modification in piping, instrumentation, and operating conditions of the system producing this material. The design safety engineer should examine inventories of all materials very critically to assure the safest and best design.

CASE HISTORY NO. 731

Modified Double Base Slurry Explosion

Description: At approximately 6:00 P.M. on August 25, 1961, an explosion occurred at a Naval facility involving a classified formulation of modified double-base propellant slurry, which resulted in instant death of five civilian workers.

The building in which the explosion occurred was approximately 50 feet in length, divided into two sections by a 10-ft. corridor extending the length of the building. On either side of this corridor were cubicles approximately 10 x 10 feet with 1-foot-thick reinforced concrete walls. The open sides of the cubicles faced outward from the corridor walls. The explosion occurred in the second cubicle from the front of the building, on the right-hand side. The first cubicle on this side was used for weighing and preparation of ingredients contained in the propellant mix. This second cubicle (in which the explosion occurred) contained a 50-gallon Baker-Perkins type mixer located approximately 3 feet from the walls, in one corner of the cubicle. The controls for this mixer were located on the wall of a transverse corridor separating this pair of cubicles from a similar pair of cubicles which contained no explosive at the time of the incident. A similar type concrete structure used for the same purpose is located approximately 300 feet from the open ends of these cubicles. These two buildings were separated by an intervening earth barricade.

The water-jacketed type mixer contained modified double base propellant. No desensitizers were used in this special formulation as it was being mixed in slurry form. The cooling water in the jacket was maintained at 60-65 degrees Fahrenheit. At the end of the mix, the water was to hold this temperature until the mixer was emptied in order to prevent the material from "setting up." Following the mixing operation, the mixer was stopped, the mix lid removed, and the material removed by vacuum from the mixer to a casting container alongside the mixer. Approximately 200 pounds had been removed, leaving an approximate 15-25 pounds for manual removal. Manual removal is by scrapedown with non-sparking type spatulas and transfer to the casting container. The explosion occurred during removal of the remaining 15-25 pounds from the mixer. It appears that, in the scrapedown operation, a considerable amount of propellant was adjacent to the power shaft end of the mixer. A portion of this shaft with flange minus sigma blades weighing approximately 40-50 pounds, was propelled almost vertically from the cubicle and penetrated the roof of a building 700 feet away. The escape of this fragment, and its trajectory, indicate the likelihood that the original explosion occurred within the mixer and in all probability, adjacent to the flanged portion of the shaft and then communicated to the casting can alongside the mixer. The casting can contained approximately 200 pounds of propellant.

Four of the operators were within the mixing cubicle, or its doorway, and the fifth operator was in the control cubicle adjacent to the mix cubicle.

The roof of the building in which the explosion occurred was transite, as well as a building located approximately 300 feet distant. These transite roofs were a complete loss and were practically removed from both buildings. Likewise, the closure to the open ends of the cubicles in both buildings were transite and had wooden doors. The transite was blown apart, and in many instances, the doors were split and pulled from their hinges. The only major structural damage was to the cubicles on the right side of the building in which the explosion occurred. Two sides of the mixing cubicle walls were completely blown apart and other walls were blown down or left standing at an angle. There was no major structural damage to the left corridor wall or any of the cubicles on the left side of this building.

The Navy is suspending the process development stage of the slurry casting process for a close re-examination. It is anticipated that this re-examination will involve a restudy in the laboratory (particularly as concerning high-energy propellants) for better characterization of the safety aspects of the various processing steps.

(Editor's note: The above has been made available to MCA by The Armed Services Explosives Safety Board.)

CASE HISTORY NO. 732

Molten Metal Fire--Burn

Description: The employee was melting magnesium-lithium scrap. While using a skimming tool to push a piece of scrap down into the molten metal, the skimmer slipped off the scrap into the molten metal. Molten metal splashed out of the pot onto the front of his bib overalls (flame retardant). He attempted to hold the burning metal and overalls away from his body with his gloved hands as he went to the safety shower. The employee received moderate burns to both hands, thighs and lower abdomen.

Cause:

1. Regular fire-proofed clothing provides inadequate protection from splashes of molten magnesium-lithium alloys.
2. The thin edge of the skimming tool was unstable when placed on the edge of the piece of scrap being melted.
3. The employee was using his left hand to hold the skimmer (normally right handed) to push down stock with some force toward him, resulting in splash in his direction. (The employee was holding a scoop of flux in his right hand to extinguish any flame started by disturbance of the surface of the molten metal.)

Preventive Measures:

1. In addition to regular fire-proofed clothing, all employees working with magnesium-lithium alloys will be provided with leather aprons.
2. The special handling techniques of melting different alloys will be reviewed with all molten metal handlers.

CASE HISTORY NO. 733

Rotameter Guard Shattered

Description: While an operator was checking on the flow of material through a rotameter, it ruptured with sufficient force to break the Lucite guard spraying a dilute hydrofluoric acid solution over his face, chest, arms and legs; his monogogles preventing serious eye injury. The provided Lucite guard shattered and proved inadequate under the 45-pound pressure. The glass rotameter which broke had a designed pressure of 185 pounds.

Cause: The exact cause of the rotameter's breaking has not been conclusively determined.

Preventive Measures: The glass tube rotameter has been replaced with a metal tube type rotameter and a check valve has been installed between the eductor and the rotameter.

Editor's Comment: Glass is not generally used in contact with hydrofluoric acid in any concentration.

CASE HISTORY NO. 734

Nitroglycerin Stability Test

Description: A technologist was carrying out a stability test on nitroglycerin and on mixtures of nitroglycerin with various materials. Eight loosely stoppered 6-inch test tubes were immersed in an oil bath at 82°C. The oil bath was contained in a stainless steel beaker heated by an electric mantle. After the test had been underway for some time, a small puff of smoke appeared in one of the tubes. A detonation occurred immediately involving all tubes, a total of 20 to 25 grams of nitroglycerin. The technologist sustained a fractured elbow and fractures and lacerations of several fingers.

Cause: Test equipment was not shielded.

Preventive Measures: The heating bath will be redesigned and adequate shielding will be provided before the test is run again.

CASE HISTORY NO. 735

Splattered with Hot Molten Metal

Description: An employee was adding scrap to the furnace. Some of this scrap contained wet saw chips. The furnace erupted, throwing droplets of molten metal and splattered the employee inflicting multiple burns. He continued to work for over a month when it was found necessary to do a skin graft to a burn on his foot. He was hospitalized and will lose 3 to 4 weeks' time.

Cause: A steam explosion resulted when moist scrap came in contact with the hot and molten metal.

Preventive Measures:

1. Provide adequate means of predrying scrap before dumping into the charge bins.
2. The present practice is to feed scrap early in the charge and bring the furnace to required level with virgin metal.
3. The use of improved or additional personal protective equipment for casters will be investigated.
4. A survey of other casting operations in the local area will be made to learn how to handle wet scrap.

CASE HISTORY NO. 736

Poor Communication

Description: A pipefitter, using a pipe-cutter, cut into a 1-inch liquid hydrocarbon line which was under approximately 100 psig of pressure. The pipefitter, upon noticing a pin-hole leak, stopped the job before there was any equipment damage or injury to personnel.

Before this revised hydrocarbon pipe system was put in service, it was necessary for a 1-inch line in this system to be separated from the feed header. The supervisor instructed the pipefitter, pointing out the line to the craftsman and told him that it had been vented and prepared for cutting. The craftsman misunderstood which pipe was to be cut and proceeded to cut a pipe which was in service.

Cause: The supervisor did not clearly designate which pipe was to be cut. These pipe lines were approximately 12 feet from the ground and immediately below the open grating on the compressor house catwalk.

The pipefitter, believing that he understood which pipe was to be cut, did not question the instructions.

Preventive Measures: Both the supervisor and the craftsman have been reinstructed on the proper procedure for such work and their responsibility to fully communicate and understand the job instructions. Other maintenance supervisors and craftsmen have been informed of this incident through their regular safety meetings.

CASE HISTORY NO. 737

Tried to Re-Chock Moving Freight Car

Description: Employee and co-workers were unloading a freight car of coal at the Power House. The hand brake was set and one wheel chocked with a piece of 4 x 4. Due to vibration from the car shaker, the brake released and the chock fell off the track. When the car started moving, the employee ran to the front of the car, crossed the track in front of the car, grasped the chock and placed it back under the wheel. In so doing his left hand was caught between the wheel and the chock. These unsafe acts resulted in a compound fracture of the left ring finger and an estimated temporary total disability of 42 days.

Cause: Unsafe work methods permitted to continue uncorrected. The practice and hazard was not detected and corrected by supervision prior to the accident, although similar run-aways had occurred before.

Preventive Measures:

1. Since this injury, a more positive holding device in the form of a two-wheel chock has been designed.
2. A cable and holding clamp has been made for attachment to the cars in the event other methods fail. One end of the cable is secured to a concrete post.
3. All railroad cars, especially those being either loaded or unloaded, should be kept under positive control. Setting brakes and chocking with sticks and stones is not adequate. Rail clamps, either the "M & M" or Aldon should be used. In some cases a cable with suitable clamps to secure framework of car to track may be more feasible.

CASE HISTORY NO. 738

Improper Use of Lift Truck

Description: A fork lift driver was transporting a coil of metal on a sleeve with a fork lift truck. The restraining band either broke or slipped off the coil, and the coil started to unwind. When he realized the coil was loose, he stopped the truck suddenly and the truck tipped forward. The coil slid off the end of the forks and the truck leveled itself. The top front edge of the battery case struck the employee's back when the truck returned to a level position. He received a contusion of his left elbow and a fractured vertebra.

Cause: Carried load too high. Load too heavy. Stopped too quickly.

Preventive Measures:

1. All loads will be carried as close to the floor as practicable.
2. When a sudden stop is necessary one should drop the load to the floor as well as apply the brake. All drivers have been advised accordingly.
3. A survey is in process to determine the maximum size and weight of load that can be carried on each lift truck.
4. Other methods of moving materials within the mill are under study.

CASE HISTORY NO. 739

Drains Plugged with Adipic Acid--Worker Scalded

Description: At about 4:50 p.m., a senior operator reported that a floor drain on the second floor was still plugged despite the fact that a steam lance had been left steaming out the drain for almost 24 hours. (The drain had been apparently plugged on the previous day by molten adipic acid which had leaked from a flowmeter drain valve on the third floor and had solidified in four floor drains on the second floor; three of the drains were readily unplugged by melting of the adipic acid, using a flow of steam from a lance connected to a 175 psi steam header.) He and the foreman inspected the floor drain to determine if it was feasible for Maintenance to remove the drain line and rod it out; this was decided against as it seemed to be a major job. The continued steaming had resulted in a pool of condensate about 2 inches deep over the drain and about 8 to 10 feet in diameter which, in effect, was cooling the steam before it could melt the adipic acid. An attempt was made to increase the steam flow to such a rate that the condensate could not run back into the drain as fast as it was blown out. Then, the operator, under the supervision of the foreman, pushed a mop over the drain to prevent the condensate from running back into the drain and to subject some pressure to the blocked line. The operator's helper, who was operating the steam valve from about 20 feet away, was directed by the operator to close the steam valve. However, before this could be done, steam and condensate blew out around the mop and doused the operator's legs with steam condensate. After removal of clothing from the affected area, he was taken to the medical department before transferring to the hospital.

The Investigating Committee visited the scene of the accident and discussed details with the injured man's foreman, the Building Supervisor, and with the Maintenance foreman for the area involved.

Discussion with the Maintenance foreman brought out the fact that the drain was eventually unplugged by Maintenance the next day after about six hours of steaming. Removal of condensate was accomplished using a siphon apparatus. He said that plugging of the drains with adipic acid is a fairly common occurrence and is usually handled with no difficulty by Production operators. In this case, however, the drain was later found to contain substantial quantities of trash, including insulation, welding beads, and welding rod left by construction which probably added considerably to the difficulty of the job.

The injured man's foreman admitted that the accident was the result of poor job planning and impatience with the slow steaming procedure. He also cited the lack of cleanout plugs on the floor drains as being a contributing cause of the accident.

The Building Supervisor indicated that the personnel involved are very experienced and competent in their job. He also stated that because of the adipic acid spill the day before, he had left instructions to clean up the area, and this may have been the reason for the perseverance exhibited.

In the investigation, it was determined that the plugged drain was not impeding production in any way and the average crew would have left it for Maintenance. The Committee feels that the injured and his foreman took the plugged floor drain as a challenge and without thinking of the consequences, proceeded to do the job.

Cause: The basic cause of the accident was use of the improper method of doing work. Although not covered specifically in the Safety Manual, common sense dictates that any time pressure is required to unplug a pipeline, a definite physical connection should be made. The entire system should be designed to handle the pressures involved.

Contributing causes were selected as follows:

1. After the normal clean-out procedure was unsuccessful, the job should have been turned over to the Maintenance Department. The responsibility for repairing the drain was improperly assumed – it could have been repaired by Maintenance on the following day with little inconvenience.

2. The decision to pressurize the drain line was made hastily with no thought as to the possible consequences.

3. The lack of clean-out plugs can be considered as a contributing cause of the accident. However, since the Maintenance Department can unplug the drains with their special equipment, the Committee feels that there is no justification for installation of clean-out plugs on the existing equipment unless it can be economically justified by the Engineering Department.

Preventive Measures:

1. It should be emphasized that when a job requires special equipment, don't improvise unless all the possible consequences have been clearly understood.

2. In all operations involving cleaning of lines and vessels with steam, compressed air, etc., if pressure is required to free the obstruction, always make a physical connection which has been designed for the pressure to be used. Pressure should never be applied to non-rated vessels or lines.

3. If routine repairs which are normally performed by operating personnel are not effective or successful, the Maintenance Department should be requested to do the job.

CASE HISTORY NO. 740

Human Failure

Description and Cause: An employee sustained chemical burns of both eyes and the back of the neck and a fellow worker was burned on the nose, left arm and both legs when sprayed with an approximate 62 per cent silver nitrate solution.

At the time of the accident, the two injured men were changing the filter in a pump discharge pipe above a tank. Department rules require all switches to be locked out; however, the workers had failed to provide themselves with this protection. The worker receiving the eye injuries was standing on a ladder adjacent to the tank and was looking up toward the filter to see that it was in proper alignment. The other worker was on top of the tank, assembling the two portions of the filter body. As this was being done, a third employee descended an adjacent stairway, walked past the two men working on the filters without noticing them and turned on the switch controlling the pump supplying the filters. The men were in plain sight from the switch location and not over eight feet away. As the silver nitrate solution sprayed out, he shut the switch off, but the two men working on the filter were already splashed.

The injured men then climbed down to the floor, one pulled an adjacent safety shower and flooded himself with water. The more seriously injured man used an eye bath but went to the locker room upstairs to shower. Safety glasses with sideshields were being worn by both men and although one received burns of the eyes, safety glasses prevented more serious injury to both.

The worker receiving the eye injuries was transferred to the hospital for treatment. The eye physician stated that no permanent impairment should result from the burns.

Preventive Measures: The following lessons can be learned from this incident:

1. Whenever maintenance work is to be done on chemical piping, equipment, or apparatus, all switches controlling pumps, valves, etc., should be locked out.

2. If sectional control valves are available in the piping system being worked on, they too should be closed as an additional precautionary measure.

3. Operators in chemical process areas must be constantly on the alert for other employees who may be working nearby.

The Industrial Safety Department is reviewing the eye protection standards of the department with supervision in order to recommend better protection.

CASE HISTORY NO. 741

Built-in Trouble

Description: While employee was operating a Servall Ommi-Mixer (Serial No. 264) at 14,000 r.p.m., he noticed that the mixing vessel was unscrewing from the apparatus. He turned the power off with his right hand and reached for the vessel with his left hand. The vessel fell as he reached for it and his hand was carried into the whirling blades which caused severe multiple lacerations of his left middle finger.

Cause: Improper design of the vessel which permitted the torque of the swirling liquid to tend to unscrew the vessel.

Preventive Measures: The Mixer has been enclosed, with controls on the outside and a microswitch on the door.

CASE HISTORY NO. 742

Ignition of Toluene Vapor by Electrostatic Spark

Description: An employee was transferring toluene by vacuum from a 55-gallon drum to a kettle through a 1/4-inch plastic tube. The tubing at the drum end was fitted with a flannel filter (held in place by two turns of copper wire) in order to prevent contamination of the kettle with scale from the drum. When the desired amount of toluene had been transferred, the employee pulled the tube from the drum. At this time, vapors ignited and enveloped the area around the bung opening of the drum. The employee received moderate burns on the left wrist and hand.

Cause: A thorough investigation after the fire revealed the following:

1. The toluene drum was not grounded.
2. The copper wire holding the flannel in place had two antenna-like projections.
3. Both ends of the drum were bulged after the fire.
4. Plastic tubing is a nonconductor of static charges.
5. The toluene drum was 1/4 full after transfer was made.

From the above facts, the following conclusions were made:

1. As the toluene passed through the plastic tube, a static charge was built up on the tube.
2. The static charge collected on the antenna-like projections of the copper wire.
3. The toluene vapors around the bung opening of the drum were within their explosive limits.
4. As the tube was pulled from the drums, there was a static discharge, with a spark, from the copper wire to the edge of the bung opening of the drum, causing ignition of the toluene vapors. This, in turn, was followed by a flash fire outside the drum and an explosion inside the drum.
5. Had the drum ruptured, the accident would have resulted in a much more serious fire and injury.

Preventive Measures: Transfer tubes will be made of stainless steel and grounded. Operators will be reinstructed to make sure the grounds on the kettle and drums are secure.

CASE HISTORY NO. 743

Pressure Rupture--Potassium Compounds

Description: A laboratory technician was heating a 5-liter round-bottom flask containing about three liters of solidified still heel containing potassium compounds among other materials. The lower part of the flask was in a heating mantle; the upper, wrapped in aluminum foil. The material in the bottom of the flask apparently melted and generated steam pressure which could not escape through the solid upper crust. When the flask ruptured, the hot materials gushed into the hood and out through the open window of the hood into the aisle, striking the technician who was stooping over making an adjustment on an electrical control outside the hood. He sustained burns of his face, neck, shoulder, and arm.

Cause: Insufficient shielding.

Preventive Measures: The need for a second shield, such as plastic, around the equipment inside the hood, is being re-emphasized.

CASE HISTORY NO. 744

Acetylene Cylinder Fire

Description: Two men were searching for a Freon leak in an air conditioning system. They were preparing to check for the leak by passing an acetylene flame over the equipment. When the leak is found, the flame changes color. A small 40 cu.ft. cylinder of acetylene was being used for this purpose. A regulator, hose and torch were attached to the outlet valve. The men opened the valve, and one of them lit his cigarette lighter for the purpose of igniting the torch. As he did this, there was a blinding flash and a flame shot out of the cylinder up to the ceiling. The men managed to extinguish the blaze with a CO_2 extinguisher and carried the cylinder to the adjacent roof where the vapors were allowed to dissipate. There was no injury or damage.

Cause: The fusible plug on the cylinder let loose either from previous damage or perhaps because the cigarette lighter was brought too close to it.

Preventive Measures:

1. An electronic device for detecting Freon leaks has been ordered.
2. Lead work and other pipe fitting which in the past has been carried out with small cylinders of acetylene will be converted over to natural gas.
3. It was recognized that the biggest danger in the plant from a fusible plug melting out is on the acetylene cylinders for welding equipment. Hence, special safety meetings were held for all Mechanical and Engineering people. At this meeting the construction and operation of acetylene cylinders was explained; the purpose of the fusible plug and the hazards in case one melted out were also elucidated. It was pointed out that if a fusible plug melted out and a fire ensued, that in most cases it would be better to let the fire burn and turn in the fire alarm and control the fire where the flame impinged on the building. It is not good practice to extinguish this type of fire and allow the vapors to accumulate inside the building where an explosion might occur. Of course, if the vapors fail to catch fire, the only alternative is to remove the cylinder outside with all possible speed.

CASE HISTORY NO. 745

Mixture Exploded During Mixing Process

Description: Explosion occurred in mechanical mix wing of pyrotechnic area on February 21, 1961, during mixing boron-potassium nitrate igniter composition of the following formula: 3257 grams boron, 9362 grams potassium nitrate, 989 grams laminac and 500 grams trichloroethylene. The igniter composition was being mixed in Simpson Intensive Mixer by remote control, utilizing mix-muller principle. The boron, laminac and trichloroethylene had been mixed through a mixing cycle of 10 minutes. The operator poured the potassium nitrate on top of the pre-mix, retired to the operator's station, and started the mixer for a 20-minute mixing cycle. After the mixer had been in operation for approximately 5 minutes, an explosion occurred. A supervisor received second degree burns on the left hand. Three light fixtures and interconnecting electric conduit, air control system of room door and mechanical linkage of room door damaged. All paint burned off. The present design and layout of the mechanical mix wing room is inadequate for mixing large batches of hot compositions. The flame from the explosion flashed around the edge of the door of the mixing room which caused the injury involved in the incident. The flame flashed through a 12-inch reinforced concrete wall, around an electrical conduit, into an adjacent room, leaving burned residue on the ceiling and on glass blocks near floor level and next to the door of the room. The air-operated door of the room came open some time after the incident and prior to arrival of fire protection division personnel, and when the door opened, the interlock switch shut off the mixer. The flame flashed through a conduit port in the wall, bouncing off the back wall of the mechanical mix wing. The supervisor of the operation stated that he had checked operation of the mixer, via the vision port, just prior to the explosion and everything was normal.

Cause: Exact cause undetermined but possible causes are:

1. The mullers and scrapers of the mixer may have got out of adjustment allowing them to ride on the bottom of the mixer, which could cause friction, initiating the decomposition.
2. The laminac binder may have built up on the muller, and could rub the bottom of the mixer, causing enough friction to initiate the decomposition.
3. Composition may have built up at the edge of the dumping door, which could have been pinched by the scraper passing over it.
4. Composition may have been pinched between moving parts of the mix-muller assembly.

Preventive Measures:

1. The batch size for mixing in the mechanical mix wing should be limited to a maximum of 15 lbs.

2. The inner doors of the room should be modified to prevent flash arounds.

3. Light wood or transite blow-out doors should be installed on all rooms of the mechanical mix wing.

4. Door controls inside the mechanical mix rooms should be enclosed in boxes to prevent the possibility of pressure from explosions opening the room doors.

5. Mullers and scrapers of mixers should be gauged at the start of each shift to assure that adequate clearance is maintained.

6. The mixer should be modified to facilitate remote control dumping.

CASE HISTORY NO. 746

Methyl Bromide Tank Explosion

Description: At approximately 8:25 P.M., the methyl bromide storage tank exploded. The explosion split the tank and literally turned the cylindrical section inside out. A few pieces of the tank wall were detached; the largest piece was hurled approximately 750 feet. Placement of the piece between existing equipment indicates a nearly vertical descent. Damage to the building consisted of considerable glass breakage, shattered transite siding and structural damage.

Three men were working in the area at the time of the explosion. One was knocked unconscious momentarily and suffered superficial glass cuts on both hands and his left ear; the other two men were virtually uninjured.

Plant personnel who were present at the time of the blast reported: 1. They heard a hissing (whistle) just before the explosion; 2. They saw a cloud of gas erupt. The cloud was orange; it turned brownish and then dark as it floated away.

Pertinent facts of incidents prior to the explosion:

1. During the afternoon of the day of the explosion, nearly fifty cylinders of methyl bromide were filled from the tank; at 3:45 P.M., the valve on the air line was turned off, the pressure on the tank at that time being 175 psig.

2. The tank, 38 feet long and 52-1/2 inches inside diameter with a wall thickness of 7/8 inch, was 1/3 full of methyl bromide. The specifications on this tank permitted the use of 375 psi safety valve setting and called for a 500 psi hydrostatic test. Periodic inspections, the most recent in March of this year, have indicated the absence of corrosion and that the tank was in good repair. Because the methyl bromide service called for only 200 psi pressure, the tank was tested to only 300 psi hydrostatically earlier this year. The safety valve was set for 225 psig and had recently been tested.

3. At the time of inspection, a sight glass level gauge was removed because of the danger of breakage, and a magnetic float gauge installed.

4. Methyl bromide filling operations have been handled in this manner since 1944.

Cause: The investigation revealed that the methyl bromide was not contaminated; the methyl bromide-air vapor in the tank was explosive; and the thermo-dynamics of the methyl bromide-air reaction was sufficient to burst the tank.

In 1928, the U.S. Bureau of Mines found the explosive limits of methyl bromide to be 14.0 ± 0.5% in air at atmospheric pressure. Recent work indicates a considerably broader range at higher pressures. Under the conditions present at the time of the explosion (20^{o}C, 175 psig), the vapor in the tank would contain 13.7% methyl bromide, well within the explosive range.

There are several possible ignition sources which include: static spark, and methyl alumi-

num bromide. The first possibility, static discharge, was discussed with the U.S. Bureau of Mines. Based on the history of methyl bromide and the construction of the piping of the tank, in this instance static discharge as the cause of the explosion is considered remote.

A much more probable ignition source lies in the second alternative. In March 1961, a level gauge was installed in the loading tank. In August, the gauge ceased to function. The construction of the gauge includes an aluminum tube which extends 18 inches into the tank mid-way on the end of the tank. The seals at each end of the tube are not sufficiently tight to prevent methyl bromide from filling the tube when submersed in the liquid. In the complete absence of oxygen, aluminum reacts with methyl bromide to form ethyl aluminum bromide, a pyrophoric material; when this material is exposed to oxygen, it ignites spontaneously with considerable heat. The following reactions have been suggested:

$$2\ Al + 3\ CH_3\ Br \longrightarrow (CH_3)_2\ Al\ Br + CH_3\ Al\ Br_2$$

$$(CH_3)_2\ Al\ Br + O_2 \longrightarrow (CH_3O)_2\ Al\ Br \text{ Exothermic}$$

$$2CH_3\ Al\ Br_2 + O_2 \longrightarrow 2CH_3O\ Al\ Br_2 \text{ Exothermic}$$

Investigation showed the level gauge mounting to be still intact in the tank wall. Approximately two inches of the aluminum tube was still attached. The outside surface of the tube was smooth and uncorroded while the interior was severely pitted, one pit extended through the tubing wall. Since the formation of methyl aluminum bromide is very remote in the presence of oxygen, it is theorized the tube filled with methyl bromide, the oxygen became depleted, and the reaction began. When the level of the methyl bromide dropped in the tank, the methyl bromide in the tube slowly drained out exposing methyl aluminum bromide to the explosive air-methyl bromide mixture. The heat of reaction would be sufficient to ignite this mixture according to the following equation:

$$4\ CH_3\ Br + 7O_2 \longrightarrow 2Br_2 + 4CO_2 + 6H_2O$$

Thermo-dynamic calculations indicate the reaction of methyl bromide and air under the conditions which existed in the tank (20°C, 175 psig) would produce a temperature of 2500-2600°C and a pressure of 1900 psi. A gas pressure of this magnitude would stress the tank walls to a point of failure.

Preventive Measures:

1. Air is no longer being used to transfer methyl bromide or pressurize cylinders or tanks. Presently, notrogen has been substituted in all phases of the operation.

2. The engineering and production departments have been alerted to the dangers of bringing nonferrous metals in contact with halogenated compounds.

3. Users of methyl bromide have been warned as to its explosive hazards.

CASE HISTORY NO. 747

Unstable Nitroso Chloride Derivative--Laboratory Incident

Description: The use of nitroso chloride as a reagent for the preparation of solid derivatives of olefins, has been known for a great many years and has been of especially great value in the characterization of certain members of the Terpene series. An accident occurred involving one of these nitroso chlorides which may serve as a warning to other workers in the field.

The nitroso chloride of alphamethylstyrene was prepared by treating a mixture of the olefin and amyl nitrate with concentrated hydrochloric acid in the usual manner (Hickenbottom, Reactions of Organic Compounds, pg. 28). The bluish white crystalline product was filtered off, washed with several portions of methyl alcohol and dried in air. The dry product was placed in an 8-oz. wide-mouth screw-capped bottle. The following morning, while working in the laboratory, a hissing noise was heard coming from the direction of the bottle of nitroso chloride. Turning around, white smoke was observed escaping from the cap of the bottle. The employee immediately left the laboratory and closed the door. A few seconds later there was a loud report and the room became filled with white smoke. After the fume hood had cleared the room of smoke, it was re-entered so that the damage might be surveyed. The bottle had remained upright and intact but the Bakelite cap had been broken into several fragments which were scattered about the room. The contents of the bottle which had been transformed to a black resinous material, had been thrown against the ceiling and over the desk. In addition to the black resinous material, there was some yellow granular substance which was probably only partially decomposed nitroso chloride.

Cause: From the nature of the report and the fact that the bottle was unbroken, it seemed unlikely that a detonation had occurred. Apparently, the nitroso chloride had been undergoing slow decomposition for some time and finally the heat evolved or decomposition products accumulated to the point that the reaction was accelerated and sufficient pressure was built up to force the cap from the bottle.

Preventive Measures: It is suggested that nitroso chloride be prepared only in small quantities and that they should be destroyed as soon as they have been used.

CASE HISTORY NO. 748

Xylene-Petroleum Naphtha Vapors Ignite While Loading Centrifuge

Description: A crystalline intermediate is separated from a 50-50 mixture of xylene and petroleum naphtha by dropping from an overhead crystallizer into a centrifuge via a stainless steel line. The centrifuge is a 32-inch suspended basket (overdriven) type. Exhaust ventilation is connected to the casing which effectively prevents escape of vapors to the surroundings.

On this day, two of the seven centrifuge loads in the batch had been successfully processed. During the third drop, a flash fire occurred in the centrifuge basket. The flames forced the operator from the platform before he could close the valve on the drop line from the crystallizer. This permitted approximately 300 gallons of mixed solvents to flow into the burning basket. Sixty seven sprinkler heads opened in this two story building, effectively minimizing damage in the building. Flaming solvent was floated out of the building doors adjacent to the centrifuge and into a sewer pipe trench. Fire spread in the trench for approximately 300 yards and broke a twelve inch ceramic chemical waste pipe in the trench, adding fuel to the fire.

Despite the intense flames, damage was minor and the fire in the building and in the trench was brought under control in a very short period. There were no injuries.

Cause: The operator stated that this batch was extremely grainy and that the cake had built up along the bottom of the centrifuge basket to a point where it was almost touching the nozzle on the petroleum naphtha wash line. Since this particular mixture had given indications that high charges of static eletricity do accumulate, it was felt that the cake had become charged and arced to the ground wash line, igniting solvent vapors.

Preventive Measures:

1. The process was changed to eliminate the use of petroleum naphtha in the crystallizer and as a cake wash. Despite the fact that the equipment was bonded and grounded, it is difficult to prevent static accumulations in centrifuges and where this is a problem, the only safe solution is to change the process or use a different type of extractor.

2. Drop line valves to centrifuges, filter pots and similar pieces of equipment will be provided with either self closing valves, heat activated valves, or extension handles as the situation requires.

CASE HISTORY NO. 749

Two Boron Hydride Incidents

(A) Decaborane-Polyethylene Bag--Static Charge--Fire

Description: A fire occurred in a test area when a technician was working with decaborane. He had removed a scoop full of the material from a drum and had placed it in a polyethylene bag on a work table approximately one and a half feet away from the drum. He heard what he described as a "snap" or "crackling" noise as the material in the bag burst into flame. He evacuated the room immediately.

Fire spread from the bag to the drum, then to another full bag on the floor next to the drum. The fire was extinguished by an overhead automatic sprinkler system. Heat from the fire was intense enough to actuate three of the four sprinkler heads in the room.

The technician was wearing prescribed protective equipment, i.e., conductive-sole shoes, flame-proof coveralls, canister-type respirator, and neoprene gloves. In addition, the drum of decaborane was an approved storage and transport container, and the floor was of concrete treated for conductivity. (Incidentally, the conductivity of the floor had passed satisfactory inspection only three days before the incident.) Nevertheless, the technician did receive burns on the hand from the heat of the fire and accumulation of decaborane dust on the glove before he could remove the glove. Due to the rapid actuation of the automatic sprinkler system, damage to the building and equipment was slight.

Cause: It is believed that a static charge built up on the scoop and discharged to the polyethylene bag, passed through the decaborane dust in the bag and ignited it.

Preventive Measures: It is recommended: (a) in operations with decaborane and similar hazardous materials, that the drum, scoop and bags be physically bonded by a metal band strap that terminates at a ground point common to the entire building; (b) that personnel wear face shields, in addition to safety glasses; and (c) that comprehensive S.O.P.'s be prepared to cover the entire operation.

(B) Pentaborane Exposure Symptoms

Description: Two men reacted with what appeared to be toxicosis from pentaborane after exposure during a disposal operation. The two employees were cleaning out a cylinder of pentaborane; they are men regularly assigned to disposal operations. A charcoal bed was not used in this instance; however, the men observed the disposal was progressing as expected, and they noted no unusual reaction. Total time of exposure to pentaborane was a one-and-a-half-minute maximum. Approximately an hour following the disposal operation, both men began to experience a "queasy" feeling. Other difficulties were experienced with psychomotor functions, in memory blocking, lack of coordination, feelings of detachment, and related quasi-psychotic reactions demonstrating the "classic" symptoms of borane toxicosis. The incident occurred on Thursday; neither victim was rational until Sunday. However, recovery was complete, and there is no evidence of permanent physical or mental impairment.

CASE HISTORY NO. 750

Explosion Inside Dry Box

Description: A laboratory employee was working with an organo lithium compound in a dry box. He was holding a small glass flask, containing about 0.1 gram of material, by the neck, in his left hand. As he approached the flask with a spatula in his right hand, there was an explosion. The employee received moderate to severe lacerations in the palm of his left hand as well as on the little and ring fingers.

Cause: It is believed that the explosion was due to a static discharge between the spatula and the glass flask or the small amount of material in the flask.

Preventive Measures:

1. This incident resulted in short, shielded tongs being made up for use inside of a dry box. Also a shielded spatula has been made up for use in this type of work.
2. The need to limit the quantities of unknown potentially hazardous materials in dry box work has been reviewed with all concerned.
3. Additional flexible transparent plastic (Ethyl Cellulose) shielding is being considered for use inside of the dry box, including a piece on the inside of the dry box cover glass in the area through which the operator looks to do his work.
4. All employees have been encouraged to use polyethylene equipment to reduce potential tissue damage when parts of the body are exposed to an explosion.

CASE HISTORY NO. 751

The Foreman Didn't Wear Goggles

Description: The foreman was supervising the removal of a sight glass on the recirculation line of a chemical mixer. He had instructed his men to wear safety goggles but neglected to wear his own personal protective equipment.

The mechanics were removing the bolts that held the metal ring that holds the glass against a flange in the piping when the electricians inverted the rotation of the gear pump. This evidently caused the glass to fly out and hit the wall. One of the broken pieces of glass struck the foreman's left eyeball. As a result of this accident, it was necessary to remove the man's eye.

Cause: There was a lack of coordination between the departments. The foreman neglected to wear the eye protection provided.

Preventive Measures: Supervision has again been instructed on their responsibility to always plan each job, to analyze the hazards involved and to coordinate the job with each department and each workman involved. Particular emphasis is placed on supervision observing their own personal safety and always setting the good example by personally using the protective equipment provided.

CASE HISTORY NO. 752

Chlorine Truck Rams Phenol Tanker

Description: A near-miss accident occurred when a truck carrying six cylinders of chlorine rolled into a tanker of phenol which was being unloaded.

The phenol tanker was positioned by the tractor driver who had towed it, and a chock was placed in front of one of the front wheels to prevent rolling. A second chock was subsequently placed in front of one of the rear wheels.

The tanker which contained approximately 900 gallons of phenol at 60-70°C was sampled by a member of Plant Study Department. The foreman coupled up the tanker and proceeded to unload, using rubber hoses and compressed air.

The truck carrying the chlorine arrived and stopped about 10 feet from the phenol tanker since it could not be unloaded until the phenol was transferred to the storage and the tanker removed. Total weight of the truck and chlorine was about 14 tons. There was a slight down-slope from the truck to the phenol tanker.

A drum cradle from the melter was on the road opposite the chlorine bay, and this was moved by the three persons present (including the truck driver) thus diverting their attention. During this period, the truck rolled into the phenol tanker pushing it until the unloading hose and air line were fully extended. The transfer was stopped, and the truck moved, the phenol tanker pushed back into position and unloading completed. The truck received some damage from the collision. The fact that the unloading hose was relatively new and special non-slip couplings to secure the hose to the vessel and the tanker were recently fitted prevented either a broken unloading line or one of the couplings failing. In either event, hot phenol would have sprayed the area. With the exception of the formalin tanker which is fitted with a brake, the usual procedure with tankers throughout the company is to chock the wheels to prevent rolling.

Cause:

1. The truck carrying the chlorine was not adequately braked and was parked in such a position that it could collide with the phenol tanker.

2. Chocking is only adequate to prevent rolling under own weight and not suitable to withstand external force.

Preventive Measures:

1. Adopt a general rule that under similar conditions, trucks at unloading points are not parked on a collision course.

2. Where hoses are used for either loading or unloading purposes, insure that secure and adequate couplings are used.

3. Carry out regular inspections of hoses used for these purposes.

4. Use warning signs marked "Danger Tanker Unloading."

5. Supervisors involved in the loading or unloading of tankers should insure that adequate safety precautions concerning the tankers are carried out.

6. Use more efficient chocks.

7. Check the hand brakes of all trucks.

CASE HISTORY NO. 753

Tank Entry Permit Signed Prematurely

Description: In a continuous process, raw materials enter Nos. 2 and 3 neutralizers and the resultant mass flows into a steamer where the mass is sparged with steam and then flows into a finisher. Wet SO_2 gas is evolved from the neutralizer and the steamer. Headers carry this gas to the acidifiers and through coolers to Department F-223. Condensate from the headers and coolers is returned to the steamer.

The department was shut down and the neutralizers and steamer washed out. Repairs and inspections of the neutralizers and header system were made during the day shift. The SO_2 headers were open at several places and washed. Work in the steamer was delayed because additional washing of this tank was necessary.

The Department 223 crude room foreman signed the field inspection of the tank entering permit for the steamer, leaving it in the drawer of the crude room chief operator's desk. He then left the plant to take his wife to the hospital.

The permit was put in place sometime prior to the shift change (4:00 p.m.). However, by the time the tank was entered, work on the header system was complete and the blind ends and previously removed spools were back in place. The large diaphragm valves in the header were closed as were valves in all header drain lines except one which has no valve.

A laborer entered the tank (for final cleaning before repairs by shop personnel) at approximately 4:40 p.m. He used a ladder for descent. The manhole is small (10 1/2 x 10 1/2 inches) and required entry with arms overhead. The ladder was then removed from the tank to allow passage of a bucket. He reported that conditions were hot but tolerable to his watcher and to the middle shift chief operator.

After about eight buckets of sludge were removed, the laborer called for the ladder and said that liquid sprayed on him and that the SO_2 was bad. The ladder was not lowered because the laborer (choking) immediately climbed up the air hose. The watcher grabbed him but lost his grip due to slippery gloves and SO_2 coming out of the tank and the laborer dropped into the tank again. On climbing up the air hose again, the watcher got a good grip on him but could not get him through the manhole. At this time, another employee came up the stairs and quickly sizing up the situation, assisted in working the laborer's shoulders through the manhole and helped lay him on the grating floor.

The laborer was apparently unconscious and gagging. The shift supervisor pulled his tongue forward and removed mucous from his mouth to clear breathing passages. The night superintendent arrived shortly thereafter, administered oxygen and took him to the dispensary on a stretcher. From there, he was sent to the hospital for observation.

Who attached the tank entering permit to the tank has not been determined. Witnesses established that it was on the tank at 3:00 p.m. and when entry was made.

The source of SO_2 gas and the liquid has also not been determined, but its source was probably the SO_2 header system.

Cause: The primary cause of this accident was that tank entering permit procedures were not strictly followed. The permit was signed prematurely. Wrist harness was not worn by person entering the tank. Piping conditions changed between inspection and actual entry. Also noted during this inspection was that valves closed for the shutdown were not tagged.

Preventive Measures: It is recommended that tank entering and tagging procedures be thoroughly reviewed with all supervisory and hourly personnel.

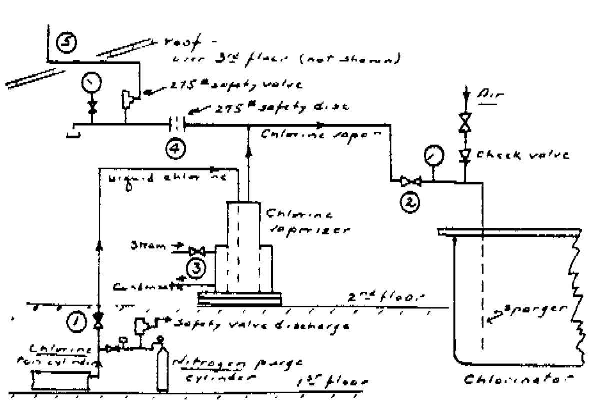
CASE HISTORY NO. 754

Chlorine Leakage

Description: Chlorine gas escaped into the shop work area through a ruptured gasket in the safety disc flanged holder (4). (See sketch) Two men working in the area suffered respiratory irritations from the gas. Prompt action by the shop foreman and a maintenance mechanic in evacuating the area prevented more serious injuries.

Prior to the incident, the main steam supply line to the area had been shut off for maintenance repairs. As a result, the chlorination operation was interrupted since there was no heat available for the chlorine vaporizer. The operator shut off the chlorine vapor feed valve (2) at the chlorinator and the steam valve at the vaporizer (3). Approximately one hour later, the maintenance work was completed and the main steam supply restored. The operator opened the steam valve (3) at the vaporizer to preheat the vaporizer before resuming the chlorine feed flow. Within five minutes, the gasket (4) failed and a large release of chlorine filled the area. The operator immediately shut off the cylinder valve (1) while the mechanic notified the foreman and helped evacuate other personnel.

The system is protected by a safety disc and safety valve in series with each set at 275 psi. Investigation showed that the safety disc had blown from the pressure developed in the system. The pressure could not release, however, through the safety valve because the safety valve discharge line was plugged at an elbow (5). There is doubt that the safety valve was in good order since a subsequent test showed it did not release until under a 600 psi pressure. Consequently, the safety disc gasket ruptured and the excess vented into the shop.



Cause: 1. The chlorine system should have been completely shut off during the steam shut-down period. The operating instructions did not cover the steps to be followed in the event of interrupted service.

2. The safety disc apparently leaked causing corrosion of the safety valve seat which prohibited discharge of the safety valve at 275 psi.

3. The safety valve discharge vent was plugged. Inspection procedures for detecting such conditions were inadequate.

Preventive Measures: 1. The procedure for shutting down the chlorine feed for short periods will be rewritten to include purging of the line.

2. The log sheets for the process will be revised to provide for recording the pressure in the safety disc-safety valve assembly on each batch.

3. A new two inch vent has been installed to replace the one inch line and periodic inspections of the complete vent line will be established in accordance with Safety Standard S-11, Inspection of Pressure Relief Devices.

CASE HISTORY NO. 755

Contact with Aniline Causes Poisoning

Description: An order was submitted by Production to repair the condenser on No. 11 reactor, Flectol H Department. The condenser had three small holes in the side of the shell about two-thirds of the way down. The mechanical repair order was passed on to the maintenance foreman through the planner. The foreman checked the job site and requested the operator to drain the condenser so the repairs could be made. When the mechanics arrived at the job site to perform the work, they found that the condenser had not been drained. One of the mechanics went to the control room to request the operator to drain the condenser. The operator told the mechanic that the condenser had been repaired in the past (without having to drain it) by using metal screws. The injured attempted to repair the condenser in this manner, but was unsuccessful due to the material flowing from the holes. (While attempting to repair the condenser, the injured's cloth gloves became saturated and were discarded. The other mechanic suggested that rubber gloves be used, but the injured believed that they would have been of little use due to the location of holes which allowed the material to spill out onto his arms.) Being unable to make the repairs, the mechanics notified their foreman that it would have to be drained. The maintenance foreman requested the production forman to have the operator drain the condenser. The injured felt that there was aniline in the spillage since he had encountered a tingling sensation in his hands. Being smoke-break time, he went to the area shop while the condenser was supposedly being drained. After smoke-break, the mechanics and foreman returned to the building. The production foreman was at the building instructing the operator to drain the condenser. The injured mentioned to the production foreman that he thought he had been exposed to aniline. The production foreman sampled the material and informed the injured that there was aniline present. The mechanics proceeded to repair the condenser after it was drained. After the repair was completed, the mechanics entered the control room. By this time, the injured showed evidence of aniline toxicity by the change in his complexion. The production foreman sent him to the dispensary for treatment.

Cause: Exposure to aniline liquid and vapors which was due to:

1. Lack of protective equipment (rubber gloves).

2. Lack of proper preparation of job site.

3. Lack of knowledge of contents of spillage. (Poor communications between responsible persons.)

Preventive Measures: 1. Production to inform Maintenance of hazards of process when submitting request for the work by:

(a) More information being submitted when an order is called in so the mechanical repair order will "spell out the hazards of the job".

(b) The maintenance foreman and production foreman should discuss the job line-up to insure the equipment is prepared for the work when working on process equipment.

2. Building 34 to publish a notice of the hazards of their department and present to Maintenance so a review can be held with the mechanics.

3. Maintenance foremen to insure proper protective equipment is used by the mechanic when working on process equipment.

4. Re-issue the data sheets on toxic chemicals issued by the July-August, 1960 Safety Committee. These are to be used as reference sheets by all foremen when exposure is likely.

5. Review with plant personnel the fundamental rules for working with chemicals as issued by the Safety Committee.

6. This investigation is to be discussed with all plant personnel so proper action can be taken through better design, operations and maintenance to prevent an occurrence of this type from happening within another department in the plant.

CASE HISTORY NO. 756

Catalyst Hot Spot

Description: A reaction system was set up on a lattice rack for the isomerization of an organic chloride. An electric mantle was used to heat the two liter flask, which was vented through a glass tube filled with granular cuprous chloride in firebrick. A condenser and product pot were installed after the catalyst bed. The catalyst bed was heated by an asbestos wrapped nichrome wire.

The reaction appeared to be going smoothly when suddenly a flash occurred and the flask ruptured. The burning liquid contents sprayed out over the immediate work area. Burning droplets sprayed and fell on two men in the area. Both received scattered burns. One received burns which required skin grafting.

Cause: It is believed that a hot spot in the catalyst bed (300°C at time of flash) caused decomposition, an immediate pressure rise and a flash back into the flask.

Preventive Measures: 1. Adequate flash shielding around reaction equipment is to be provided.

2. Flame resistant laboratory coats are being placed in use for all research and development personnel.

3. Further study as to the cause of the hot spot in the catalyst bed is to be made.

CASE HISTORY NO. 757

Powder Ignited When Hopper Fell

Description: An employee had moved a hopper of powder into the Screen House and hooked it to an air-operated hoist. As he raised the hopper, it hit the limit switch but the switch failed to operate. This caused the cable to break and the hopper started to fall. The employee saw this and started to run toward the door but was enveloped by flames when the hopper hit the floor and the powder ignited. Ignition of the powder was caused by impact or heat generated when the hopper bottom was pierced by landing on a sharp edge of the tram car.

The Standard Operating Procedure requires that this hoist be operated from the second floor of the building after raising the hopper part way. This allows the hopper to be raised without going into the limit switch. Had the employee been operating the hoist from the second floor, he may have avoided the limit switch. Even though the hoist had gone through the limit switch and sheared the cable, the employee would have had a better avenue of escape by using an escape chute provided on this floor.

Cause: (a) Failure to follow Standing Operating Procedure.

(b) Failure of Hoist Limit Switch.

Preventive Measures:

1. The Standard Operating Procedures will be re-emphasized to all operating personnel.
2. Operating procedures will be revised to include a daily check by operating personnel of all safety devices and cable condition.
3. All hoists have been re-inspected for cable wear and properly functioning limit switches.
4. The use of fire-resistant clothing on all dry operations will be investigated.
5. The practicality of remote control during the hoisting phase of this operation will be investigated. If remote control is not practical, a secondary limit switch arrangement will be studied.
6. The operating height of this hoist will be increased so that it will not be necessary to raise the load so close to the limit switch during normal operations.

CASE HISTORY NO. 758

Reaction Kettle Explosion

Description: On Saturday night at about 10 p.m., a series of explosions occurred in the vicinity of the esterification kettle. Although there were no injuries, the explosions demolished the kettle room, ruptured natural gas lines and hurled the kettle and associated components (estimated projectile weight 6000-7000 pounds) a distance of 340 feet. Fires resulting from escaping gas caused extensive damage to the adjacent building and its contents. Most of the fire damage was caused by escaping gas.

The direct gas-fired kettle was last fired 40 hours before the explosion. Warm "intermediate" material was transferred to the kettle between 14 and 30 hours before the explosion. The kettle room was last entered 13-1/2 hours before the explosion and the plant last occupied 5-1/2 hours previous to the explosion.

Physical examination of the evidence and testimony of witnesses led to the conclusion that the incident was triggered by a rapid increase in pressure and temperature within the kettle. No evidence was found to indicate the rise of pressure and temperature was caused by conditions external to the kettle.

The material involved in this accident was a polyether-alcohol, made by the reaction of a mixture of propylene oxide and ethylene oxide with a polyhydric alcohol.

Investigation: Both chemical analyses and infrared examination did not reveal any significant differences between samples of the batch in question and earlier production of the same product. Particular examination was made for peroxides and for epoxides.

A laboratory study was undertaken to determine the product's inherent thermal stability. Conditions which were varied included temperature, pressure, surface area, air versus nitrogen atmosphere, sample size and accidental additives.

No high velocity (brisant) decomposition could be made to take place, but it was found possible to cause rapid decomposition with the generation of substantial heat and pressure, which in a closed vessel could exceed its bursting strength. Two sets of conditions were found which could lead to exothermic decomposition. The first is an oxidizing process, whereby air (or chemical oxidizing agents such as hydrogen peroxide) reacts with the polyether-alcohol rupturing chains and producing volatile oxidized products. The speed of the reaction is a function of the surface area and temperature. If surface area is large, rapid temperature rises can occur as low as 100°C.

The second condition is in the absence of air or other oxidizing agent. Rapid exothermic decomposition does not occur below 300°C. At slightly above 300°C an exothermic decomposition occurs producing substantial quantities of gaseous products. Pressure appears to favor the decomposition reaction.

Rapid air oxidation with a substantial temperature rise was found to occur with other ethylene oxide and propylene oxide adducts. Furthermore, exothermic decomposition in the absence of air was found to take place for other ethylene oxide adducts at initial temperatures between 300 and 350°C.

Conclusions: It is known that the product was pumped to the kettle at slightly over 100°C and remained there for a number of hours without agitation. The charge was exposed to air at the surface since a vent line was open. In the course of nearly half a day, the temperature rise perhaps would be sufficient to raise the temperature of some of the product above 300°C. At this point, a rapid exothermic decomposition, not requiring air, would commence and would sustain itself and generate more and more heat and gaseous products until the kettle ruptured. This is believed to be a reasonable explanation, based on sound chemical principles, of the known facts of the accident.

Preventive Measures:

1. Avoid prolonged elevated temperature storage of ethylene oxide or propylene oxide adducts.
2. Provide means for agitation of vessels containing such products.
3. Protect ethylene oxide and propylene oxide adducts against air, particularly at elevated temperatures.
4. Install recording thermometers equipped with alarms on storage and reaction vessels.
5. Consider the use of anti-oxidants to stabilize such products.

CASE HISTORY NO. 759

Flammable Vapor Inside Centrifuge Explodes

Description: The centrifuge had previously been charged with a full cake of purified phenacetin and the alcoholic mother liquors spun off. The operator then proceeded with the spray washing of the cake, using hot ethyl alcohol - water (80:20) wash solution.

Normally, the wash solution is used at room temperature; but in this instance, a new solution freshly prepared from hot, freshly distilled ethyl alcohol was used without being allowed to cool.

The spray washing was completed and the cake was being spun to reduce the moisture content before unloading. The cake had been spinning for approximately 15 minutes when the operator heard metallic scraping sounds coming from the centrifuge. He immediately shut off the power, applied the brake and brought the basket almost to a stop.

The operator then turned away from the centrifuge to go and examine the solvent discharge pipe and the sump to find out whether the centrifuge had finished draining. At this point, a loud explosion occurred inside the centrifuge. The force of the explosion blew open the hinged cover and flames shot out, striking the operator on the right side of the face and neck. The hinged cover fell closed again, following the explosion.

The injured operator recovered himself and pulled the cover open again, while other operators and supervision used extinguishers and water hoses to prevent re-ignition of the solvent.

The foregoing description of the accident is based on the testimony of the injured operator and nearby witnesses. The injured operator was wearing safety spectacles at the time, which probably prevented more severe injury around the eyes.

The investigating committee ordered the centrifuge partially dismantled and then examined the interior, and the parts, to determine the cause of the metallic scraping sounds reported by the operator. Circular marks of abrasion were found on the top rim of the centrifuge basket and these matched corresponding abrasions on the splash ring on the underside of the centrifuge cover. There was evidence of repeated contact in this area and in some sections the metal surfaces had been blued by frictional heat.

Further examination of the reassembled unit showed that when the cover was in place, the splash ring cleared the top rim of the basket by approximately 1/16- to 1/8-inch. A comparison was drawn between the clearances in this instance and a clearance of 1 inch on a similar model centrifuge in the Research Pilot Plant.

There was also evidence indicating that on some previous occasion, not within memory of anyone contacted, the bolting flange of the cover had approximately 5/8-inch cut from it and new bolt holes drilled. This, in effect, permitted the cover to be mounted and the splash ring to position itself within 1/8-inch of the rim of the basket.

The shaft bearings were checked for wobble and end play and appeared satisfactory.

Electrostatic grounding of the entire assembly was checked with an ohmeter. The electrical resistance of the unit was less than 1 ohm.

It was concluded that either a minor imbalance in the centrifuge cake or flexing of the basket or shell at high speed would have been sufficient to spoil the clearance between the splash ring and the rotating basket, thus permitting metal to metal contact and abrasion.

Cause: In the opinion of the Investigating Committee, the fire and explosion was caused by metal to metal contact and abrasion of the rapidly rotating centrifuge basket with the fixed splash ring on the underside of the fixed cover. The evidence showed that considerable heat was generated by this contact with the possible evolution of sparks.

The metal to metal contact was made possible by the cutting and refitting of the bolting flange on the centrifuge cover at some previous date.

The heat generated and/or the sparks evolved ignited the mixture of air and ethyl alcohol vapors within the confines of the centrifuge shell, causing a flash fire and explosion.

Preventive Measures: 1. That the clearance between the rim of the basket and the splash ring on the underside of the cover be restored to one inch. This work is already in progress.

2. That the use of warm or hot solvents in the centrifuge be discontinued, or special precautions be taken when they must be used.

3. That a liquid seal, such as a dip leg, be installed on the discharge pipe from the centrifuge, where it enters the solvent collecting sump. Although this feature had no bearing on this accident, it is considered an essential safety device.

4. That a suitable carbon dioxide purge and blanketing system be designed and installed on the centrifuge, to be used to render an inert atmosphere in the centrifuge at any time flammable solvents are being used.

CASE HISTORY NO. 760

Acid Tank-Truck Pressurized When Cover-Clamp Failed

Description: A truck driver was unloading his third tank load of 60° Baume sulfuric acid during the middle shift. (A second driver had already unloaded three truck loads of the same material.) He followed the customary procedure of connecting the 3-inch discharge line from the truck to the line going to the storage tank. He connected the air supply to the 3/4-inch air connection on top of the truck. He turned on the air supply, observed that the pressure gauge indicated 22 psi. After one or two minutes, he entered the truck cab to work on his log sheet. He had just picked up the log when he heard a "rumbling" from the tank that resembled the sound made when live steam is discharged into the bottom of a tank of water. It was quickly followed by a vibration of chattering noise and then a loud bang.

He started to leave the cab, but stayed in when he discovered acid spraying down heavily in the area surrounding the truck. When the acid stopped falling, he went to the air supply shed and turned off the air. He called the shift superintendent, who thereafter called in the Materials Handling Supervisor.

A 30 x 60 ft. area around the truck was wet with acid, some laying in sizeable puddles. The driver estimated that 150 gallons had come out. The hinged loading nozzle cover was open, but the swing bolt assembly was laying in the roadway some 40 feet away, torn off at the weld. The level of acid in the truck was about 12 inches below the top.

Cause: The cause of the accident was the failure of the loading nozzle cover hold-down mechanism, probably due to inadequate design and a weakening by corrosion.

Discussion of Investigation: The following facts were established:

1. The air supply system was functioning properly, the relief valve relieving at 28 psig. There was no evidence of excessive moisture in the air supply.

2. The vent on the storage tank was open.

3. The storage tank had previously had 60° acid in it, and all of the loads of acid transported during the evening of the accident analyzed 60°.

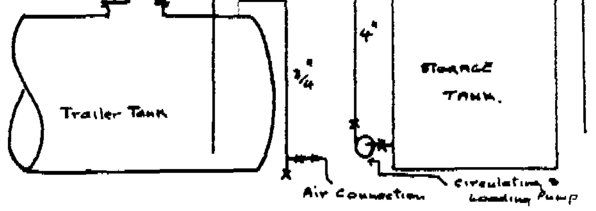
4. The circulating pump was valved off, and there is no reason to believe it could have inadvertently been started up.

5. The manhole cover and loading nozzle cover showed considerable corrosion; the weld that failed appeared particularly corroded.

6. There was no evidence of failure to follow approved procedures.

The committee considered the possibilities of a violent reaction from contaminated or mixed acids or the introduction of water. It considered the possibility of a hydrogen explosion set off by a static charge. None of these possibilities seemed likely in view of the conditions.

The most likely explanation is the simplest, that the loading nozzle swing bolt failed first on one weld, causing air release and chattering, followed by failure of the other weld. The blowing open of the cover was followed by the sweep of



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air out of the opening. At the same time, the acid in the 6-inch pipe line flowed back into the tank under its 12 or 15 psi static head causing enough surface disturbance to let a sizeable amount of acid be carried up into the air.

It should be noted that the 2-inch lead rupture disc on the manhole did not rupture. The exact rupture pressure of this disc is not known as it is cut from lead sheet on demand. This disc does fail occasionally at normal or slightly above normal blowing pressure. The lack of failure in this case tends to verify the weakness of the cover clamp.

Preventive Measures: Specific - The following primary actions are recommended:

1. Expedite the completion of approved project for the installation of facilities to allow use of a pump for acid unloading.

2. Alter the loading nozzle cover on the two acid trucks to include three swing clamps 120° apart.

3. Investigate to see that ICC regulations in regard to pressure testing of trailer tanks are being complied with.

4. Determine the proper thickness of lead for the rupture disc. Provide this information to the shift superintendents.

Although not directly related to the accident, the following secondary recommendation is made:

1. Install a properly drained concrete pad at the tank truck loading spot.

CASE HISTORY NO. 761

Safety Harness Saves Scaffold Workers

At about 9:15 a.m. two construction men were working off a swinging scaffold about 35 feet above ground level on the east wall of the building. Both of these men were working near the north end of the scaffold, rubbing down the concrete floor beam at the third level. Both men were wearing safety harness with lifeline attached.

One man attempted to pass the other on the scaffold by placing both his feet against the side rail of the scaffold and pushing with his back against the building wall. When he pushed against the scaffold, it swung out away from the building and both men fell off the scaffold and dropped about three feet before being stopped by their lifelines.

A third man saw the accident and rushed to the second floor of the building and climbed up a scaffold to where he could reach these men to see if they were injured. He then assisted them to get back on the scaffold and climb into the third floor.

Both men were sent to the medical department, but were uninjured.

This accident calls to attention the absolute necessity of following the plant safety regulations which state that no one shall work off a swinging scaffold without a safety harness with lifeline attached.

This case totals five individuals who have been saved from serious falls due to use of safety belts and lifelines.

CASE HISTORY NO. 762

Standing in Front of the Gun

Description: Standard procedure for cleaning the vent system of four sodamide reactors was being followed: (1) Nitrogen purging, (2) Installation of blanks at each reactor, (3) Removal of a large nozzle cover on the seal tank, and (4) steaming off the system.

Several seconds after a pipefitter removed the nozzle cover, an explosion of unknown cause occurred in the system and was relieved through the open nozzle. The pipefitter, who was standing partially in front of the nozzle sustained severe burns on his lower right leg; operating foremen and another employee who were standing nearby received minor burns.

Cause: Probable cause of the explosion is a hydrogen-oxygen ignition resulting from inadequate purging or the presence of explosive azides or peroxides. Cause of the severity of the injury is position assumed by the pipefitter.

Preventive Measures: The cleaning procedure is being modified to insure adequate purgging; methods of rendering possible azides or peroxides inert are being studied, and protective clothing such as asbestos suits will be worn for step 3 above in addition to step 2 unless there is a certainty that dangerous materials are not present. Employees have again been reminded to stand to the side rather than directly in front of possible trouble.

CASE HISTORY NO. 763

Pump Sprays Ammonia

Description: Two employees were changing a valve on a pump. After the inlet and discharge valves were closed, to isolate the pump, the men proceeded to pull the cover plate. As the cover plate came loose, ammonia sprayed on the men. One employee was burned on the shoulder and the other was burned on the neck.

Cause: 1. The pump contained residual pressure.

2. One of the men was not wearing a face shield.

3. The men failed to check the pressure in the pump.

Preventive Measures: 1. A vent line is being installed on the discharge line of the pump to insure venting of residual pressure.

2. To make venting more positive and to insure that no liquid ammonia remains, the pump will be run idle to vaporize the material while it is being vented.

3. Face shields will be mandatory to supplement safety glasses with side shields.

CASE HISTORY NO. 764

Eye Protection Pays Off

Description: Joe is an outside warehouseman. Most of the time he can be found at the east end of the plant. He looks after stocks of cylinders of compressed gases and keeps close watch over plant stores of Sulfuric Acid. Normally, his work consists of weighing off Sulfuric Acid into carboys and drums which are then delivered to the Manufacturing Department.

Thursday afternoon was cold. Pipefitters had just completed the unloading of a tank-car load of Sulfuric Acid 93% into one of the storage tanks. There was an unfilled order for a half dozen carboys of Sulfuric 93% waiting to be filled. Joe takes pride in keeping up with his work. Since the necessary empty carboys were on hand, he decided to refill them that afternoon.

Cause: One of the pipefitters who had been working on the tank car was standing nearby as Joe placed one of the empty carboys on the scale under the tank valve. Shortly after the acid started flowing into the carboy, there was a puff of brownish smoke and acid was sprayed up and out from the carboy and directly into his face. (Someone had violated the safety rule in using the carboy for chemicals other than Sulfuric Acid.) The pipefitter helped Joe into a nearby building where he quickly flushed his face as he removed his goggles. He then changed clothes and reported in at the dispensary.

Although Joe received numerous superficial burns about his face and neck (see picture) none of the acid got behind his goggles. His eyes were uninjured and today Joe is again as good as new. Were it not for the fact that he was protecting his eyes while working with corrosive materials, there certainly would have been a different ending to this story.

Preventive Measures: Sample taken from the broken carboy and spectrographically analyzed was inconclusive. All manufacturing departments have been reminded again of the general rule concerning use of carboys as containers for materials other than the material indicated by its label.

CASE HISTORY NO. 765

Operator Sprayed with Glacial Acetic Acid

Description: A quantity of glacial acetic acid had collected in the sump pit. The injured, a pipefitter who had been working on another unit, was asked to help hook up the discharge line on a positive displacement pump to be used to recover the acid from the pit. One end of the 3-in. suction line, equipped with foot valve and positive screen, was placed into the sump.

It was intended to recover the acid via the 3-in. intake of the displacement pump coupled to a 2-in. line into the suction inlet of a residue pump. Using a 3-in. by 1-1/2-in. reducing bushing, a 1-1/2-in. nipple, a 1-1/2-in. by 2-in. bushing and a 2-in. hose boss fitting, the 2-in. acid hose was coupled to the displacement pump, the gasoline engine was started and the pump put into operation at 10:30 a.m. At 12:15 p.m. it was shut off for lunch period.

On restarting the pump at 1:00 p.m., the motor started then stopped. On restarting and with the pump speeded up, the diaphragm ruptured. Acid sprayed on the injured and two other employees.

Cause: It is assumed that the displacement pump, prior to luncheon shutdown, was operating with reduced suction possibly caused by foreign material fouling the suction line screen. Once the obstruction dislodged, the pump, which was not equipped with a pressure release system, attempted to operate with a 3-in. suction intake against a 1-1/2-in. discharge, rupturing the diaphragm. Acid sprayed on the injured. The shift supervisor and a third man, who was helping, suffered slight acid burns.

The three men involved were wearing safety glasses and the pump was considered to be in good operating condition prior to the accident. Attempting to operate the full pump body against the restricted discharge was not recognized as unsafe.

Preventive Measures: Instructions have been issued that should it be necessary to reduce the discharge side, the suction side must be equally reduced and at no time will the use of a diaphragm pump without a pressure release system be compounded with another pump. A diaphragm or positive displacement pump (without a pressure release system) must be able to discharge a quantity of liquid equal to the quantity of intake and without restriction. Should it be necessary to use an additional pump or pumps, the diaphragm pump shall be discharged into an open vessel or other container in such a manner that no back pressure is produced.

CASE HISTORY NO. 766

Explosion of Composite Rocket Propellant During Mixing Operation

Description: On July 13, 1961, explosion occurred involving 2882 pounds of polysulphide perchlorate solid rocket propellant during mixing in a 200-gallon Baker-Perkins mixer equipped with sigma blades. Mixing was accomplished by the forward mixing method which requires the fuel to be introduced into the mixer first. The oxidizer container is then placed in position and the operators retire to the remote control building. The mixer is started and the oxidizer screw feed switch activated. Upon completion of each cycle, the mixer is stopped and the sides of the mixer bowl are scraped down to insure a homogeneous mix. The total time cycle for completion of this particular mix is 130 minutes. The mixer had operated satisfactorily through the oxidizer addition phase (40 minutes) and the mixer was stopped for removal of the oxidizer tote bin discharge chute and screen, and scraped down. After the first additive batch was introduced into the mixer, the operators retired to the remote control shelter and placed the mixer in operation. The mixer had been in operation for 64.2 minutes of the required 70-minute cycle (104.2 minutes total time), when the explosion occurred. The total amount of 2882 pounds of propellant in the mixer was consumed in the explosion. Static depth of propellant mix in mixer at time of explosion was approximately 30 inches and temperature of mix at time of explosion was approximately 134°F. Eleven operators working inside adjacent buildings suffered first-aid injuries from flying debris caused by the blast. All were released for return to duty (no lost time). Damage resulting from explosion consisted of complete destruction of all equipment within the mixing bay, complete severance of concrete and earth dividing walls, destruction of the mixer building and structural damage to eleven adjacent buildings.

Cause: Exact cause unknown: Probable causes:

1. Frictional heat build-up igniting the fuel-oxidizer mixture in the packing gland rings.
2. Friction as a result of metal-to-metal contact in the area where the mixer blade shaft passes through the sidewalls of the mixer (scoring of the mixer blade bearing surfaces was noted in these areas).
3. Pinching of propellant where metal separation was noted on the mixer blade shafts in the packing gland area (metal separation or "crazing" was noted on the chrome-hardened surfaces of the front mixer blade shaft in the packing gland area).

Comments: Maintenance records indicated that repacking of all four packing glands was accomplished 15 days prior to the incident. The packing material utilized in the glands is jute, impregnated with liquid polymer. Clearances between mixer blade shafts and bowl ends were checked at the time the glands were repacked and found to be within acceptable tolerances. The mixer cover was constructed of 1/4 x 2 x 3-inch angles welded to the sheet to provide rigidity. The weight of the mixer cover (75 pounds) and type of construction tended to confine the initial pressures and probably contributed to the severity of the explosion. Disassembly and inspection of mixer for worn parts and examination of blades was required annually or every 2000 operating hours, whichever occurred first. Records showed that mixer was put into operational status approximately 1 year and 2 months prior to the explosion. The required disassembly and inspection was not accomplished during this period.

Preventive Measures:

1. Blades and other moving parts of new mixers shall be carefully inspected (X-ray, magnaflux, etc.) for cracks, crevices and other imperfections before being placed in operation. Inspections will also be performed on a routine basis, not less frequent than once annually, and after each accident which results in damage to the mixer.
2. Mixer covers shall be designed to provide immediate venting in event of a fire in the mixer.

3. Standing operating procedures for maintenance of explosives operating equipment should be observed at all times.

4. Temperature recording devices should be provided for the packing gland and bearing areas of the mixer-blade shafts.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 767

Regular Operator Absent--Substitute Injured

Description: A coater operator was threading cellophane through the lacquer pan and between the "squeeze rolls." Before the employee could withdraw his right arm from the lacquer pan, another employee activated the hydraulic lever which controls the raising and lowering of the lacquer pan. The lacquer pan raised slowly but the employee's right arm was caught before the other employee could lower the pan. Employee received lacerations of the right arm at elbow and severed small artery.

Cause: Unsafe Act: Using equipment unsafely--haste.
Unsafe Condition: Unguarded machinery.
Supervisory Responsibility: Instruction and training inadequate.

Absenteeism necessitated the use of an inexperienced man for threading the coating machine. Sometimes the entire operation is done by one man who must move out of the danger zone in order to close the pan. In this case the inexperienced man was being helped by another employee who assumed the injured man was clear of the lacquer pan.

Preventive Measures: Thorough instruction and training of all employees, emphasizing the hazards around each machine and the necessary steps that must be taken to avoid injury. Operational and design improvements should be considered.

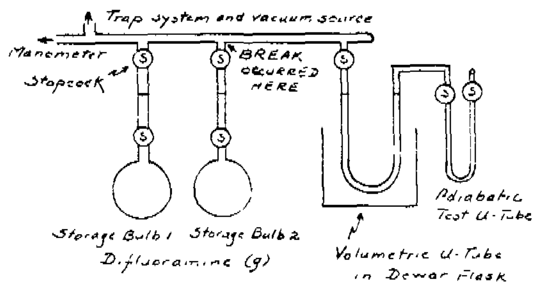
CASE HISTORY NO. 768

Laboratory Explosion of Difluoramine

At approximately 3:15 p.m., a small explosion occurred in a test bay. The accident occurred during an adiabatic compression sensitivity test on difluoramine. A schematic diagram of the test apparatus is shown. The first step in the operation requires that difluoramine gas be condensed under reduced pressure in the volumetric U-tube which is maintained at -80°C, utilizing a methylene chloride-dry ice bath. At the time of the accident, the difluoramine gas which was in Bulb 1 had been transferred to the volumetric U-tube (1.5 ml liquid) and the bulb was closed off from the system. The chemist, while standing behind a portable safety shield but reaching around its side, was turning the stopcock with a 4 ft. reach-rod to open Bulb 2 to the system. The glass line broke at the manifold (the point indicated in the diagram) while the stopcock was being turned. The bulb fell to the concrete deck and exploded on impact. Immediately the volumetric U-tube exploded. This may have been caused by the shock of the first explosion or by air rushing into the broken vacuum line.

The incident did not result in damage to the building. It did, however, completely destroy the expendable glass portion of the laboratory test apparatus. The chemist conducting the experiment received minor cuts on the arms and face and a chemical burn on one arm. The facial cuts were apparently caused by glass traveling upward from the floor and were suffered even though the chemist was wearing safety glasses and a full face shield.

Loading Apparatus for Adiabatic
Compression Test of Difluoramine



Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 769

Operator Burned by Molten Caustic

Description: The employee had been filling drums with molten caustic when the scales became fouled with solidified caustic from a leaking valve on the fill line. After the valve had been replaced, he filled about two drums and attempted to wash the caustic off the scales from the operating platform with a water hose. This was unsuccessful, so the operator decided to go behind the protective screen to be able to wash the conveyor more effectively. To do so, he stopped the pump with the emergency STOP button, placed an empty drum under the fill line and opened the fill valve in order to drain the line. He then stepped onto the conveyor beside the drum, squatted down and proceeded to wash the conveyor. The pump was not stopped as he supposed, the drum filled and molten caustic overflowed the drum and splashed onto the man, burning the operator's forehead and four fingers of the left hand. The pump was stopped by an Instrument man who saw what was happening.

Cause:

1. Possibility that the stop switch failed to function in this one instance.
2. Established procedure of unplugging and "Red Tagging" the cord was not done.
3. Routine short cuts may have become justifiable in the mind of the individual.

Preventive Measures:

1. Plug-in receptacle for the caustic pump will be moved to a position near the operating station.
2. A warning light will be installed to indicate that the pump is energized.
3. The written procedures have been revised to include disconnecting the pump.

CASE HISTORY NO. 770

Acid Splash

Description: An "outside" acid truck driver was splashed with 20° Baume hydrochloric acid about the face, eyes and chest. The accident occurred on top of the truck platform as the driver was disconnecting the hitch on the acid hose delivery line. At the time of the accident, the man was alone in the area of the unloading station. He made his own way, a distance of approximately 100 ft. and was placed under a safety shower by the employees.

Cause: The truck driver violated the plant rule that outside drivers neither connect nor disconnect to company storage tanks. The acid is unloaded from the tank truck by blowing with air. The driver disconnected the transfer hose before the air pressure had been completely vented. Although the transfer line valve was closed it was faulty, permitting residual acid to spray out when the hose was disconnected. The driver was not wearing goggles.

Preventive Measures:

1. The Purchasing and Traffic Departments have notified the carrier to insist that their truck drivers observe the plant regulations.
2. The operating personnel in this area have been reinstructed that outside truck drivers are not to handle any of the unloading equipment.
3. This review is being circulated to plant supervision to show the hazards which result when "outside" truck drivers do not comply with plant regulations.

CASE HISTORY NO. 771

Battery Explosion on Fork Truck

Description: A fork truck was reported as not having any electrical power to the switch and would not operate. An employee was assigned to trouble shoot and make the necessary repairs to put the unit back into operation. His first step was to determine if he had good mechanical connections at the battery posts. To do this, he placed the blade of a large screwdriver in the split of the battery cable on the negative post, and tried to turn the cable to check looseness.

As he did this, there was an explosion, rupturing and blowing out the top of the negative post cell; this sprayed him with broken pieces of battery and battery acid (sulfuric acid). At the time of the explosion, he was looking directly down at the battery post with his face being only about eighteen inches from the terminal.

Cause: The battery acid became low in the cells which built up hydrogen gas in the void space in the battery cell. When the employee twisted on the cable connection, it caused a spark which ignited the hydrogen gas coming from the filler cap.

Preventive Measures:

1. Always check to see that the liquid level in the battery is to the full level.
2. Use only a short tool to check the battery connection. With a short tool, possibility of grounding to the body chassis will be minimized. Whenever possible, a nonmetallic tool should be used to do this job.

CMA 048362

CASE HISTORY NO. 772

Flash-fire Resulted When Mild Steel Was Struck with Hardened Aluminum Blade

Description: On September 6, 1961, a flash occurred at the feeder hopper and weigh pan while mixing dopes. A Giant Gel 40% dope had been dumped to the feeder hopper and a small amount of ingredients, primarily sulfur, was still laying along a corner and one side of the sloping weigh pan. A flash occurred when the operator "punched" a lump through the grate to the feeder hopper and just when the screen unit was placed in operation. The flash carried up into the weigh pan along the ingredients still in the pan.

Cause: Investigation revealed that the bars of the grate over the dope feeder are of mild steel. The tamp which is used to "punch" lumps through the grate is made entirely of aluminum. The blade is made of aluminum floor plate. Operators at Dope House, when questioned, stated the aluminum blade would spark when striking the steel grate at an angle. Sparking tests of the tamp blade against steel confirms that this aluminum floor plate will spark readily when it strikes steel with a glancing blow. The aluminum floor plate is believed to be of composition containing 0.25% copper, 0.60% silicon, 1.00% magnesium and 0.25% chromium. It is stated to be hardened and non-sparking and has a hardness of 95 Brinell. It is believed that a critical air-dust mixture existed in the dope feeder and that a dust flash was set off by a spark when the tamp struck the grate.

Preventive Measures: The tamp with the blade made of hard aluminum floor plate was removed from service and a tamp with a soft aluminum blade was placed back in service. (The punch with soft blade had recently been replaced by the harder aluminum to eliminate frequent replacements of the soft blade.) Recent data indicates that practically all combinations of metal couples can cause ignition of explosive atmospheres by impact. Alloys are particularly prone to cause ignitions. Sulphur is the most sensitive material in dope houses to accidental ignition. Only pure soft aluminum tips should be used on tamps in dope houses and all tools should be used with care. Steel tools are, of course, prohibited.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 773

Eruption of Hot Caustic Injures Three Men

Description: The cook pump feeder on a Washer Repulper started to come loose and hooked on the cook pump impeller. Shear pins in a coupling sheared and stopped the pump. The drive motor and reduction gear continued to operate and the chute filled up. The level of stock came up into the repulper vat causing the repulper to kick out.

The washer was shut off and the repulper was already immobilized. The supervisor asked if steam had been shut off but did not say whether he meant #4 or #5 chute. As steam had been turned off on the #4 chute, he was advised the steam was off.

Believing it could be safely unplugged, the workmen started toward their area to start unplugging. At this time a rumbling noise was heard from inside the repulper. Three of the men turned and started to get out of the area but one man was prevented by pipes and valves in the way. The fourth man, not hearing the warning, made no attempt to get out of the way.

Immediately following this loud noise hot caustic stock and steam erupted from the repulper vat.

Cause: Had the steam lines been turned off properly this accident probably would have been prevented. It is believed the steam could have heated up the stock and built up enough pressure to blow the stock up through the repulper. It was found that pressure in the line between the cook pump and the refiner mixer could cause the cook pump to rotate backwards which could have contributed to the blow-back.

Preventive Measures: Control valves have been installed on the steam lines to #4 and #5 washer. A plugging switch on the cook pump will ring a bell if the rotor stops. A backstop braking arrangement has been installed to stop the cook pump from rotating backwards. Valve has been moved so that workmen will not be trapped. Each man has been instructed on safe procedure and the procedure has been written into the Bleachery Log Book.

CASE HISTORY NO. 774

Fracturing of Thermally Stressed Casting Causes Injury

Description: The injured was performing his assigned job of processing low carbon casts in the prescribed manner. The prescribed manner was to remove the hot casts from the cooling area by the use of a fork lift after the lime slag had disintegrated, and then to dump or sweep off the lime and paint the heat number on by use of a pressurized paint can. He then stacks the cast.

Cause: While he was standing alongside a cast, spraying on the numbers, the case blew apart due to thermal stress. A large piece struck the injured, knocking him down and pinning his one leg to the floor. The heat of the cast, which was approximately 380° at the time, caused severe burns to the leg and the weight fractured the ankle.

Preventive Measures: A revised procedure for handling low carbon casts was placed into effect immediately, whereby employees will use the 15,000-pound capacity lift truck to maintain the flow of low carbon casts from the Furnace Department to the cooling racks and on to the cooling stage area. There the casts will be allowed to cool completely before close contact work is made, such as painting heat numbers, sweeping off cast, cleaning, etc.

CASE HISTORY NO. 775

Fumes Accumulate in Excavation

Description: An excavation about 8 feet deep had been made adjacent to an oleum storage building in order to repair a water line. After completion of the repairs and during backfilling the foreman went down into the excavation to check the line after the first lumps of frozen earth had been pushed into the hole. He immediately noticed acid fumes and came out complaining of slight nausea, a headache and the taste of acid. No evidence of sickness due to the fumes could be established, but as a precautionary measure he was sent home with instructions to rest. The following day he resumed his normal duties.

Cause: At about the time of the incident oleum was being run into the tank inside the oleum storage building. The acid fumes from the vent in the tank were dropping through an opening in the earth floor (the beginning of the outside excavation) and thence into the excavation outside the building. Being heavier than air, the fumes collected in the excavation.

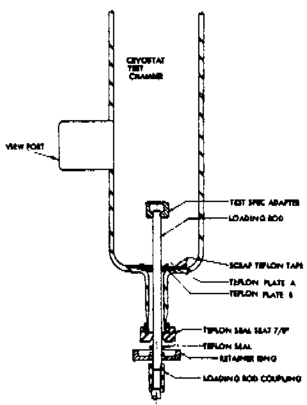
Recommendations: The potential hazard of heavy acid fumes in excavations in acid areas has been brought to the attention of all personnel.

CASE HISTORY NO. 776

Cryogenic Laboratory Fire

Description: On October 19, 1961, at approximately 2:40 P.M., a fire occurred in a hydrogen cryostat during the dismantling of associated tensile equipment. Testing was completed at approximately 2:15 P.M. At approximately 2:25 P.M. the bottom retaining ring and teflon seal were loosened. (See sketch.) The next step was to remove the lower loading rod in the test chamber. The lower loading rod coupling was frozen solidly in place. Temperature at the center of the cryostat at this time was -300°F. Test personnel used a heat gun (hot air dryer) to free the coupling. As the loading rod was being pulled up through the bottom of the cryostat, a flash fire occurred. Three test personnel received first and second degree burns on hands, arms, and face. Evidence of the fire was found as far as 4 feet from cryostat and on the outside of the cryostat, indicating fire was not confined to interior of cryostat. The test cell exhaust fan was running during this period.

Cause: This test program had been underway for approximately 4 months. Test personnel, in the interest of saving time, had bypassed Standing Operating Plan requirements for purging and bringing cryostat up to room temperature prior to entering test cell. This allowed the condition as noted to exist. It is assumed that this fire resulted from gaseous hydrogen remaining in bottom portion of cryostat, due to the failure to purge, cold temperature of cryostat increasing the gas density and poor ventilation of bottom of cryostat. The cause of ignition is assumed to be spark from or ignition by open filament of heat gun used to free loading rod coupling.



Preventive Measures:

1. Closer surveillance of all routine cryogenic operations has resulted from this incident.
2. Importance of cleanliness, purging, and Standing Operating Plan compliance was reiterated to all test personnel.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 777

Tried to Make an Adjustment Without Stopping Machine

Description: An operator was rewinding a 54-inch width master roll of .007-inch polyester film support. The thread-up of the rewinding machine included an overhead cluster of idle and rubber-covered torque rolls. The operator reached up to straighten out a turned over edge or wrinkle in the web as the support entered the cluster rolls and, in doing so, his right hand was caught between the torque roll and support. The wind-in pulled him off his feet. He grabbed for the machine frame to support himself, and kicked at the panic bar to shut down the machine. He did not reach the panic bar, but fortunately a fellow employee, observing the situation, did shut down the machine.

The injured man received a compound fracture and multiple fractures to the forearm.

Cause: In trying to straighten out the turned over edge or wrinkle, the operator violated basic safety rules:

1. Do not work on machinery while it is in motion - shut it down.

2. Keep hands out of pinch points.

Preventive Measures:

1. Instructions have been issued reminding people not to reach into moving machinery.

2. Operators will be reminded about the tensile strength of film support in general relative to paper.

3. The cluster rolls, although previously considered "guarded by location", will be guarded by an interlocked panel to prevent someone from inadvertently reaching into the roll cluster.

CASE HISTORY NO. 778

"Close Call" in Chemical Processing

Description: A man wearing conductive shoes and standing on a wet conductive floor was adjusting a de-energized heating mantle which, presumably, was also wet from moisture dripping from a condenser nearby. A second man, thinking the adjustment completed, turned on the power. The victim received enough current to freeze his hands, but he was able to break the electrical circuit by kicking the mantle plug loose from its variac. It is considered that this man escaped serious injury or death only because the variac happened to be turned low (the exact setting was not established).

Preventive Measures: Since heating mantles cannot be grounded effectively, their use in rooms with conductive floors has now been prohibited in Chemical Processing. This accident prompted a review of all electrical hazards in the group facilities; a number of other weaknesses were found, and corrections were made. No action was taken on the special problem presented by anti-static use of conductive shoes and floors, because this is a complex problem. It was questioned that the hazard of handling explosives by ungrounded personnel is as serious as the hazard of electrical shock to grounded personnel in chemical processing operations. This question may be pertinent to the chemistry laboratories for which conductive floors are being considered.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 779

Block Valve Leaked-- Operator Burned with Acid

Description: A level control flow chamber had been blocked in and turned over to maintenance with a warning that the inlet block valve to the chamber might leak. Maintenance carefully broke out both unions in the piping down stream of the valve and no leakage was evident. They then broke out the flange at the valve and found the valve plugged with process solids. While they prepared to install a blind flange on the valve, the plug blew out causing a spill which was stopped after about 10 minutes, when an operator drove a wooden plug into the valve outlet. The operator was treated in the dispensary for a minor chemical burn caused by the acid in the process spill.

Cause: Inability to completely close a block valve because of process material lodged in the valve.

Preventive Measures:

1. During the investigation, it was evident that maintenance people needed to be better informed about the hazards of chemicals handled in the area, and this will be done.

2. This particular job was being done while the unit was still in operation. In the future, supervision will carefully review jobs to determine if repair is necessary immediately or if they can be delayed until a unit shutdown is made.

CASE HISTORY NO. 780

Accident Caused by Inadequate Ground

Description: Boilermakers were installing a stop on the 2-1/2 inch extruder turntable in the research laboratory. A permit had been issued for welding in this laboratory and following normal plant practices, the boilermaker grounded the welding machine to the nearest ground which happened to be a steam line outside the building. Welding of the stop proceeded.

The extruder is mounted on a turntable consisting of a shaft and bearing mounted in the floor. All electrical wiring leading to machine is in Flex-Conduit. Water is carried in rubber hoses; and because of these conditions, there was no good return ground for the welding operation except for the four electrical conduits which are of thin-walled flexible material. Although considered adequate for grounding the machine in case of electrical shorts, the conduit could not carry the load generated by the welding machine. The smallest of the four conduits, a one-inch line, became so hot that the outside insulation melted and the wire insulation inside the conduit fused in one mass. There was no injury, but damage resulted to the electrical wiring.

Cause: Improper grounding of the welding machine.

Preventive Measures:

1. Although the National Electrical Code accepts this type of flexible conduit as being sufficient ground, additional grounding cable will be used to provide a more adequate ground.
2. This incident will be brought to the attention of all plant welders.

CASE HISTORY NO. 781

Metallic Sodium Fire and Resulting Explosion

Description: At the start of a centrifuging operation outside of the building, a valve was left open causing organic material to run onto the cement slab. Before cleaning up the spill with water, a drum was disconnected from the centrifuge, and a bung was screwed into the opening. After a short time of washing the spill with water, a fire enveloped the area. The injured employee attempted to put out the fire with a CO_2 extinguisher while his co-workers went for help. The disconnected drum alongside the centrifuge exploded causing a flash fire which surrounded the injured employee. The injured employee received moderate burns to the hands and face.

Pertinent facts of the incident prior to the explosion:

1. One step in this reaction is to add a metallic sodium dispersion into the reactor.
2. The reaction of all of the additions proceeded as planned throughout the day.
3. A sample of the reaction product was taken from the bottom of the reactor. A part of the sample was thrown on the snow so that any unreacted metallic sodium would react with water. No reaction of any type was noted. The reaction mixture was also treated with acetone - no reaction occurred. It was then decided that there was no metallic sodium present.
4. As the wheeling operation was started, the bottom outlet of the reactor was opened. (There was approximately 8-10 psig Argon on the reactor). As this was done, it was determined that the valve to feed the centrifuge was open, which allowed material to flow to the wheel and onto the floor. While this was happening, the drum on the filtrate side of the centrifuge was connected, and approximately 2-3 gallons ran into the drum.
5. The drum was disconnected from the centrifuge and a bung was screwed into the opening.
6. The operator using a service water hose washed the spilled material toward the sewer. All of a sudden, the spilled material was enveloped in flames.

Cause:

1. Metallic sodium was in the spilled material because of an incomplete reaction.
2. Water was used on metallic sodium because tests failed to show its presence.
3. The valving was not checked prior to the centrifuging operation.
4. The bunged drum in the area was heated by the fire resulting in an explosion.

Preventive Measures:

1. Develop a more adequate test and sampling procedure to determine the presence of residual metallic sodium in the final product.
2. The drums used on the filtrate part of this job will be equipped with flame arresters. Containers of flammable materials will be removed from area before cleaning up a spill.

CASE HISTORY NO. 782

Ether Explosion in Laboratory

Description: A girl chemist was distilling ether from impurities when an explosion occurred. She suffered burns of the face, hand, arm and leg.

The apparatus consisted of a distillation flask, coupled with a water-cooled condenser draining the ether into a three liter bottle. The source of heat was a single steam bath. The hood contained some extraneous equipment of which there was a thermostatically controlled hot plate with exposed contacts.

The distillation was being carried on when the chemist added more ether to the flask. A bump caused by the steam raised the flask a bit. The girl stepped over next to the hood to cut the steam back. At that moment an explosion occurred.

The explosion caused the explosion venting windows to open, but the venetian blinds were broken. A fire ensued and the girl received flash burns.

Cause: The connection between the flask and the condenser broke, permitting ether vapors to fill the hood faster than they could be removed. The vapors were ignited by the hot plate.

Preventive Measures: In order to prevent or minimize the recurrence of such an incident, the following conditions should be considered in all laboratories:

a. Sources of ignition should be removed from areas where flammable liquids can escape. Hot plates, open flames, unapproved electrical equipment, etc., are included in this category.

b. Laboratories should be designed so that it is not possible for persons to be trapped by fire.

c. Explosion venting windows should not be obstructed. Venetian blinds offer considerable resistance to explosion pressures.

d. Consider the hazards of a job and then choose the suitable conditions to carry it out.

e. Discuss new arrangements or procedures with the safety leader. His experience is valuable in recommending safe procedures.

CASE HISTORY NO. 783

Burned by Steam When Pipe Fitting Failed

Description: A pipe fitter had connected a 1/4-inch stainless steel probe through various pipe fittings to a steam hose preparatory to re-checking a sulfur pit leveling line. As he began using the probe a union parted allowing the steam hose to whip and eject steam at a fairly high pressure. As he stepped back, he tripped over the pit cover and the live steam hit him on the legs. Although he did not appear to be injured, the employee notified his foreman. Later, when blisters appeared on his ankle, he was taken to first aid for treatment. A disability of two weeks may result from this accident.

Investigation of this accident indicated that it was caused by an improperly connected union.

Preventive Measures: An engineering study will be made to determine whether or not changes in the piping arrangement would improve the present procedure. The investigation also indicated a need for improved illumination in the area and this has been provided. In addition, changes will be made in the covers of the sulfur pit to reduce the tripping hazard. This accident has been reviewed in detail at the regular shift safety huddles as part of the employee's safety training program.

CASE HISTORY NO. 784

Explosion Dinitrofluoroethane During Nitration

Description: On June 19, 1961, an explosion occurred in a small room in a corner of the nitrating building which resulted in the death of one employee and injuries to two others. The incident involved the distillation of dinitrofluoroethane (DAPHNE). This particular operation is a fractional distillation conducted at reduced pressures. The procedure involved heating the water bath from room temperature to approximately 60°C and reducing the pressure in the system to about 15mm Hg absolute. The low boiling fractions are condensed in the water cooled condenser and the distillant collected in a receiver cooled by dry ice and acetone. All vapors not condensing are passed through two cold traps connected in series prior to reaching the vacuum pump. Fractionation was accomplished in a 24-inch long glass column packed with small Berl saddles. When the vapor temperature reaches 30°C and the absolute pressure is 15mm mercury, the hot water circulating system is stopped, the vacuum pump turned off and the vacuum released. The receiving flask containing the foreshot is removed from the apparatus and the low boiling fractions collected are weighed and measured volumetrically, a new receiving flask is attached, vacuum pump started and the hot water circulating system started. The distillation is continued, and the distillate being that portion containing the main portion of DAPHNE. This particular distillation was started at 1:00 PM. At 3:45 PM the process was stopped for removal of the low boiling fractions. The vapor temperature at this time had reached 30°C as per operating instructions. At 4:30 PM the distillation was proceeding normally. At this time the pot temperature began to increase at a faster rate than the bath temperature and at 5:45 PM exceeded the bath temperature until 6:45 PM, the last recorded data available. The charge of crude DAPHNE weighed 20.74 pounds, with a volume of 7235 milliliters. Between 4:30 PM and 5:30 PM the temperature differential between the pot and the bath decreased from 12°C to 1°C with the pot temperature lower than the bath temperature and the pressure remaining at 15mm Hg absolute. Sometime between 5:00 PM and 6:00 PM the engineer was absent from the building for a period of 30 to 45 minutes. Between 5:30 PM and 5:45 PM, the pot temperature went higher than the bath temperature by 1°C and the pressure increased to 18mm Hg absolute, an increase of 3mm Hg, which indicated an exothermic reaction was taking place. Between 5:45 PM and 6:45 PM, the distillation showed more signs of an exothermic reaction with the pot temperature increasing from 71°C to 79°C while the bath temperature remained at 70°C and the pressure increased from 18mm Hg absolute to 45 mm Hg absolute. Somewhere between 5:45 and 6:40, the engineer recognized the distillation was not proceeding normally and sometime between 6:40 and 6:45 he started shutting down the distillation by adding cold water from the condenser into the bath. Between 6:45 PM and 6:59 PM the bath temperature reduced to 60°C. Just before the explosion, the engineer started reducing the vacuum by purging. He was standing in front of the distillation system at the time of the explosion and the blast threw him approximately 8 feet across the room. The operator saw the flash, started to run down the passageway, but was thrown to the floor of the passageway by the blast. He recovered himself, ran to the front of the building and phoned for help. The utility man heard the glass break and a swishing sound; quickly turning around, he saw material spraying out the top of the column and ran from the building. He heard the explosion, was struck by flying material, and jumped into a ditch approximately 25 feet from the doors of the building. The engineer in charge was fatally injured. The operator received lacerations to the right ankle and back of the head. The utility man received lacerations of the right side and left hip and rupture of the right ear drum. The engineer had been working for 6 months or more with this project and had assisted in preparation of the standard operating procedure for this operation. The SOP was in the room and readily available for reference. Property damage was approximately $15,000.

Cause: Admission of air to reduce the vacuum without first cooling the flask, thus causing an explosive reaction between the air and the products of the chemical reaction. This resulted from failure to recognize in sufficient time a dangerous condition which had been developing over a period of time; and failure to follow standard operating procedure which required cooling to room temperature before reduction of the vacuum.

Preventive Measures:

1. All standard operating procedures for operations involving materials which may cause exothermic reactions will contain a section detailing action to be taken to meet emergency conditions.
2. All standard operating procedures involving experimental processes will include special safety precautions to cover that particular process.
3. Require that operations not proceeding normally be secured and that the next echelon of supervision be notified.
4. Insofar as possible, conduct all hazardous operations from behind suitable barricades.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 785

Engaged Plow--Centrifuge Running Full Speed

Description: One of the final steps in the preparation of one of the purified inorganic salts involves the centrifugation of a salt slurry. This operation is accomplished through use of a 48-inch, suspended basket, bottom unloading, Tolhorst centrifuge. The machine is operated at 442 rpm. Process slurry is pumped into the centrifuge basket through a fixed nozzle. The slurry filters freely and presents no problem in obtaining a well-balanced load permitting the machine to operate smoothly at full speed. After washing the salt and spinning to damp-dry, the machine is brought to a stop, the discharge pan at the bottom of the basket removed and then the machine is restarted at low speed. With the basket turning at 25 to 50 rpm, the plow is lowered and the loaded salt is plowed out – the salt sliding down into a steam-heated pan dryer.

This centrifuge had been loaded and washed, then left to spin damp-dry while the operator went out to lunch. Three other operators were, however, in attendance while the regular operator was away. One of these other operators, three days earlier, had been transferred from another department and currently was in training for eventual operation of the centrifuge. This trainee was 63 years old and had an unusually sensitive skin. He was transferred to this new work area because it was felt that the work involved would be less irritating and would require little physical effort. During the three-day training period, this operator trainee had observed the regular operator load, wash and plow out at least twelve machine loads. His activities were limited, however, to observation only. He had not been authorized to operate the machine.

When the pan dryer had been unloaded by another operator, but before the regular operator had returned from lunch, this trainee apparently decided to unload the machine by himself. No one saw exactly what he did. However, when the two operators who were working below the centrifugal machine platform heard a commotion, they ran upstairs and found the trainee lying on the floor seriously injured. His machine was still operating at full speed and the plow mechanism had been thoroughly wrecked.

Cause: From an examination of the area immediately following the incident, it seemed evident that the employee, for reasons unknown, had lowered the plow into the spinning basket thus causing it to engage. The hand wheel and plow control had been jerked from his hands with such violence that the back side of the plow engaged the salt, breaking the casting which held the hand wheel and plow stop-limits, thus permitting it to spin wildly. A segment of this casting apparently hit the man in his forehead, fracturing his skull. Moments after the accident, the machine was found still in operation at full speed, power was on and the pan at the bottom of the basket still in place. Examination of all fragments of the casting showed that there were no old cracks or defects. The counter-weight cable supporting the plow mechanism was twisted and was knotted badly from having been twisted by the rotating plow. The plow itself had been bent out of shape so that it no longer contacted the salt.

1. The unsafe act in this case certainly was the "unauthorized operation of machinery."

2. Due to the severity of the employe's injury, it has not been practical that he be interviewed, however, it seems possible that he may have become impatient to demonstrate that he was ready to take over operation of the machine.

3. The employee recently had been fitted with bifocal glasses including a combination hearing aid. The possibility of poor vision and/or hearing conceivably could have contributed.

Preventive Measures:

1. The Engineering Department has arranged to substitute cast steel for cast iron for the construction of the plow lever castings and hand wheel.

2. Further study will be given the problem with a view to preventing operation of the plow unless the machine has been reduced to 25 to 50 rpm.

3. Training: It is recognized that a system or procedure must be developed that will permit no one to operate equipment unless by specific consent of the foreman responsible for its operation.

4. Job Assignment: Develop a better plan for job assignment of physically limited employees to jobs that they can perform safely.

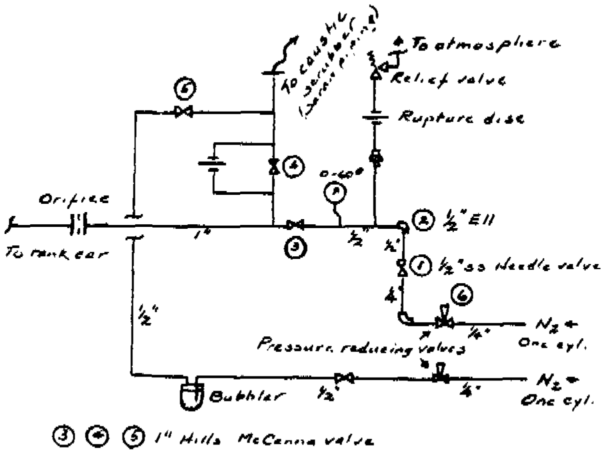
CASE HISTORY NO. 786

Burned with Bromine

Description: Mechanics started on necessary repairs to put the Bromine system in the "W" Building back into service. The system had been shut down for several months and it was necessary to replace gaskets, vent lines, valves, and thoroughly check out the system.

Mechanics were closely observed while cutting into system by supervision, and everyone was made aware of hazards when handling Bromine. Plastic gloves and gas masks were worn while initially cutting into lines.

On Friday, the morning of the accident, two pipefitters were assigned to check out the piping system for blowing Bromine from tank cars and to replace gaskets and necessary fittings and valves. As the system was already disconnected in several locations, gas masks were put aside. Shortly after lunch, they were replacing pressure reducing valve, #6 on sketch, and noticed 1/2-inch ell, marked #2 on sketch, was loose. In order to tighten this ell, it was necessary because of clearance from wall to remove needle valve marked #1 on sketch. The injured started to remove this valve, loosening it very carefully. When valve was nearly off, he wiggled it, but seeing no evidence of any liquid or fumes coming from connection, removed it. Immediately, a small portion of Bromine trapped from top of needle valve, item #1, to ell, item #2, spilled out, burning him on the forearm, wrist and hand and splashing over his clothing. Another fitter, working nearby on vent system, suffered a minor burn on his leg.



Cause: 1. Nitrogen pumping system was not considered a hazardous part of the system. (No Bromine was supposed to be present at this point.)

2. Some items of protective equipment were not used after initial break-in.

3. Gloves worn on this job did not adequately protect the hand and wrist.

4. Piping was installed so that natural pocket for material was formed.

5. There is no written procedure for shut-down of this system.

6. There is no positive method of completely purging system of Bromine.

Preventive Measures: Departmental

1. Minimum protective equipment when working on any part of the Bromine system is:
   a. Gas mask
   b. Rubber gloves (shoulder length)
   c. Rubber suit

   A full rubber suit and an air hood with an outside air supply is strongly advised, when blockages occur and pressure cannot be released. The Bromine piping is considered to be the entire system, from the nitrogen cylinder, to the tank car, to the reactor, to the caustic scrubber, to the atmospheric vent.

2. Effective Immediately. When working on the Bromine system, a Santosite - Soda ash (50:50 mixture) solution to be provided at all times to neutralize any spills in the area. Water in copious quantities should be readily available for skin contact.

3. Effective Immediately. Revise Bromine piping so that 1/2-inch needle valve, #1 on sketch, and regulating valve, #6 on sketch, are above straight section. Revise the nitrogen inlet section of piping so that any liquid will drain east towards tank car.

4. Install flange covers on all lines which carry liquid Bromine.

5. Write down specific instructions for shutting down Bromine system at the end of a run. Consider purging lines with nitrogen or some other inert medium.

General

1. All department supervision review the protective equipment requirements for similar hazards in their respective operations.

2. All Maintenance supervisors and foremen re-emphasize the fact that hazardous systems are still hazardous even after initial break-in, and safety precautions should not be relaxed at any time.

3. All departments review this accident at the next safety meeting.

CASE HISTORY NO. 787

Working with High Voltage Equipment

Description: A fatal electric shock was received by a research worker as he handled a piece of high voltage equipment. A high intensity mercury arc light source was being used to conduct a study in research. The light was approximately four inches long and 3/8-inch in diameter, held in spring action holders pressing against the ends of the lamp. Power was supplied from the secondary of a transformer (850/110 volts) furnishing as much as 1.4 amps.

The arrangement consisted of a metal box. A back cover held the lamp holders, and the leads. Investigation of the area disclosed the following conditions:

1. The box cover was dangling by the air hose (air was used to cool the lamp) against the wall. (The air was shut off.)

2. The box cover had been removed as if alterations were about to be made. (The circuit had knowingly been rewired the day of the accident.)

3. One lead was disconnected from the lamp holder post.

4. The mercury lamp was on the floor.

5. The transformer was energized.

Preventive Measures: Although the exact cause of the accident cannot be determined, there are certain fundamental principles which we all should keep in mind in working with high voltage equipment:

1. De-energize an electrical circuit when making repairs.

2. Do not work on hazardous equipment alone.

CASE HISTORY NO. 788

Horseplay

Description: The employee was burned when a fellow employee lighted a cigarette lighter near the solvent contaminated jacket which he was wearing. The injured employee received moderate burns to both hands and severe burns to one finger.

Cause:

1. Lack of awareness of the potential hazard of contaminated clothing which was fostered by previous frequent exposures to solvent.

2. Wearing a solvent soaked jacket in an allowable smoking area.

3. Horseplay—flicking a cigarette lighter at a fellow employee.

Preventive Measures:

1. (a) Develop an indoctrination program for new men that will expedite their becoming safe workmen. (b) Intensify the promotion of awareness of employee's responsibility for his own safety and the safety of his fellow workers.

2. (a) Consider the use of impervious clothing where serious exposure to hydrocarbon is possible. (b) The importance of not entering an area where a source of ignition is present while contaminated with hydrocarbons will be incorporated into the Key Points safety program.

CASE HISTORY NO. 789

Inadequate Rigging and Cramped Quarters

Description: Injured and two workmen were removing the cook-pump feeder-screw assembly in the sixth floor bleach plant. A chain block and sling was fastened to the shaft immediately inboard of the bearing pedestal and inboard of the point of balance. When the feeder screw was almost out of the casing it caught (presumably on the casing flange). When the unit was given an extra pull, the injured, who was standing in a narrow space between the unit being removed and a wooden stairway was struck on the right foot by the base of the pedestal as the unit came free, swung outwards and the heavier pedestal end dropped.

Cause: The method of rigging, while used before, was inadequate. Injured was working in cramped quarters where he was unable to step clear.

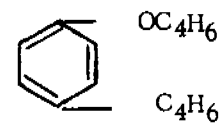
Preventive Measures: All millwright personnel have been instructed to use no less than two chainfalls at least until recommended changes have been made. A steel platform, level with bearing pedestal base so that the unit can be slid out easily, will be installed. Instructions have been issued to all plant personnel to stay clear of suspended equipment and to take extra precautions when cramped quarters cannot be avoided.

The doctor advises that this man's foot was saved because he was wearing safety shoes.

CASE HISTORY NO. 790

Experiment Backfired

Description: The reaction of butadiene with phenol in the presence of anhydrous fluoroboric acid at 60° has recently been shown to smoothly yield a mixture of ethers of type:



A similar reaction employing boron trifluoride etherate as catalyst is claimed in Australian Patent 19/7/60/62624 where the following procedure is described:

"In a stirred autoclave of 1.4 litres capacity which is cooled to 15°C, there is added a mixture of 200 gms. of petroleum ether, 94 gms. of phenol (1 mol) and 10 gms. of boron trifluoride diethyl etherate and cooled to about -10°C, 216 gms of butadiene (4 mols), cooled to about -10°C, are then added and the autoclave is immediately closed. While stirring the mixture, the temperature is allowed to rise slowly. At an external temperature of 10°C an exothermic reaction sets in so that the internal temperature is always about 3-7° above the external temperature, while the latter is allowed to rise within 8 hours from 10°C to 20-22°C. After a total of 20 hours, the reaction is complete...."

An initial attempt at duplication of this preparation was carried out in 1/4 the above scale in the absence of petroleum ether. The materials were mixed in an 8 oz. bottle at -10°C, capped and allowed to stand overnight when a viscous product still containing some solid unreacted phenol was obtained. It was assumed that a solvent was necessary to insure complete reaction and in order to obtain sufficient material for fractional distillation, four bottles each containing:

Petroleum ether (40-60^{o})	50 mls	
BF_3/Etherate	2.5 mls	
Phenol	23.5 g	(0.25 mols)
Butadiene	85 mls	(1.0 mols)

were prepared.

The capped bottles were then removed to the laboratory and at this stage consisted of a lower layer of solid phenol and an upper layer containing the butadiene, petroleum ether and presumably the BF_3 etherate. It was intended to allow the materials to shake while warming to room temperature before allowing them to stand behind screens in a fume cupboard over the weekend. At approximately 4:40, it was noticed that one bottle was warmer than anticipated and that a vigorous exothermic process was developing. All bottles were placed in the fume cupboard, the front lowered and all staff retired to a safe distance. Bottle No. 1 vented itself through gasket failure at approximately 4:45 p.m. Bottle No. 2 blew off its crown cap, while No. 3 exploded spraying its contents about the fume cupboard. No. 4 burst at 4:55 p.m. with such force that fragmentation of one armored glass panel took place. No fire followed and no personal injury was sustained.

Conclusions: Bursting pressures of 200-300 psi have been observed with similar bottles. Butadiene at 114^{o} has a vapor pressure of 300 psi and therefore a considerable and rapid temperature rise must have taken place which in a usually inadequately cooled autoclave must have been difficult to contain. Since some pressurization is essential in such reactions, incremental addition of butadiene to a solvent/phenol/catalyst system seems to provide the only safe method of approach to this reaction system, but since comparison of other patent claims with our results was the aim of the experiment, no further work with this catalyst system appears necessary.

CASE HISTORY NO. 791

Burned While Refueling Fork Lift Truck

Description: A laborer was refueling a Hyster fork lift with gasoline while the engine was running. He overfilled the tank and the spilled gasoline ignited. The employee's clothing also caught fire and he began to run. Other workmen were able to stop him and extinguish the flames. Injuries consisted of second degree burns to the back of right hand.

Preventive Measures: Instructions have been issued that all equipment is to be shut off while refueling. Signs to this effect have been placed on all gasoline tanks.

CASE HISTORY NO. 792

Explosion--Ethylene Oxide and Ammonia

A feed storage tank containing several thousand gallons of ethylene oxide exploded, injuring a number of employees and causing extensive property damage.

There were twenty-two employees involved in the accident, one of whom was injured fatally. Three were hospitalized but none are expected to suffer permanent disabilities. The remainder were taken to the hospital for treatment of cuts, bruises and minor burns or for observation.

Process equipment and buildings in the vicinity of the explosion were either destroyed or severely damaged. Blast and missiles caused destruction in areas throughout the plant, and there was structural damage, mostly glass breakage, to buildings in the neighborhood.

The explosion occurred in an ethanolamine manufacturing area which had been in operation for several years. In the process, ammonia and ethylene oxide were fed into a horizontal, tubular reactor using pumps which were interlocked to assure the desired proportion of reactants. Immediately prior to the explosion we experienced unusual variations of pressure in the unit and there are indications that during a period of high pressure, unreacted ammonia got back into the process feed tank containing ethylene oxide, resulting in a chemical reaction which caused the explosion.

Property damage is estimated at several million dollars.

CASE HISTORY NO. 793

Waste Solvent Drum Explodes

Description: An unwashed empty triethylamine drum was moved into an area between two laboratories and a funnel was placed in the 2-inch end bung opening. Static lines were connected to both funnel and drum.

Shortly thereafter, an employee working in the vicinity noted the drum smoking. He immediately turned a cold water hose on the drum. The drum contents exploded, ripping the top end nearly off and deforming the drum.

Investigation showed that in the short time between placement of the drum and the explosion, someone unknown dumped what chemical analysis indicated to be residues from a distillation containing Phosphorous Oxychloride and sulfur compounds into the drum.

Cause: It is believed that the addition of cold water to the Phosphorous Oxychloride residue could cause such an explosion.

Preventive Measures: No one was hurt, no fire occurred. Except for the drum, no damage was done. However, some real lessons can be learned:

1. Strong acids, or other extremely reactive compounds must never be placed in organic waste drums.

2. Each lab should have its own waste drum so that control can be maintained of materials being dumped.

3. Waste drums, whenever possible, should be isolated so that the person using them is protected by a concrete block wall.

4. Waste solvent drums should be vented by removing the 3/4-inch bung to relieve pressure.

CASE HISTORY NO. 794

Men Overcome In Confined Space

Description: Two men were instructed to install pipe connections to the bottom section of a 10 foot by 21 foot cone-bottom aluminum tank. One man went inside the tank while the other man remained outside. The man on the outside heard a noise as if someone had fallen into the tank. Upon investigation, he saw the man lying unconscious on the bottom. He called to a third man for help, and rushed in to rescue his fellow worker. He too fell unconscious in the tank.

Cause: Inert gas was suspected, so other workers inserted several air hoses to flush the tank. Rescue was made largely through the heroic efforts of the members of the Safety Department wearing self-contained breathing apparatus, and the quick thinking of the fellow workers. Both men were revived.

The prime causes of the accident were determined as follows:

1. Standard Safe Practices for entering tanks were disregarded.

2. The feed and return lines to the tank had not been removed or blanked off.

3. A Safe Work Permit, approved by the Operating and S and M Supervision, had not been secured.

4. An approved safety harness, with life line attached—in the hands of an outside helper, was not being used.

5. Neither ventilation nor an oxygen check had been provided. Inert gas had leaked into the tank from a pipe tied into the pneumatic conveying system at a diverter valve. Also, an eight inch return line had been tied into the pneumatic conveying system about 20 feet from the feed bin. Neither of these two lines had been blanked off from the feed bin.

6. Failure of the fellow worker to protect himself by entering the tank without adequate safeguards.

CASE HISTORY NO. 795

Burned by Steam and Hot Water

Description: The centrifuge was shut down for repairs and operating people wanted to inspect the strainer unit for wear. The operator back washed the strainer to remove any mud of phosphorus. The supervisor attempted to call out an additional operator to assist in the removing of the top of the strainer but was unable to locate the off shift operator. Since the procedure calls for two men, the supervisor said he would assist the operator in removing the strainer lid.

The operator decided to back wash the strainer again to be sure mud and phosphorus were washed out of the strainer. He closed the bottom valve and left the strainer full of water to prevent possible burning when the top of the strainer was removed. The steam valve tracing around the jacket of the strainer was cut off. The inlet and outlet pressure gauges were inoperative. He then removed the wing nuts that secure the top to the strainer jacket.

The supervisor positioned himself above the strainer jacket top on one side, and the operator positioned himself on the other side. Both were prying off the top on opposite sides using a pry bar. The side next to the supervisor broke free first, pressure released and part of the hot water in the strainer flashed to steam. Entrained water blew out and struck the supervisor. Both were wearing protective equipment called for by the job—hard hat, gloves, and goggles.

Cause: Improper Method: Opening of the strainer unit which was under pressure. Both people thought there was no pressure on the unit.

Contributing Causes:

1. Pressure gauges inoperative. No knowledge of pressure on strainer.

2. Recycle line from the strainer plugged.

3. Bottom valve on strainer closed. (Intentional to keep water in strainer to prevent possible burning.)

4. Strainer jacket was hot because of steam tracing, and the water going into jacket was approximately 85° to 90°C.

Preventive Measures:

1. Establish a written procedure including protective equipment for this job and review with all centrifuge operators. Responsibility - Department Supervisor.

2. Install vent line from bottom of strainer discharge line to the top of the feed tanks. Responsibility - Department Supervisor. To be done next shutdown.

3. Relocate valve on recycle line above present location of valve. Responsibility - Department Supervisor - To be done next shutdown.

4. Install operative pressure gauges. Responsibility - Department Supervisor - To be done next shutdown.

5. Install hook on strainer lid and proper frame for using chain fall in removing lid from a distance instead of prying off. Install hood over lid to prevent splash. Responsibility - Department Supervisor. To be done next shutdown.

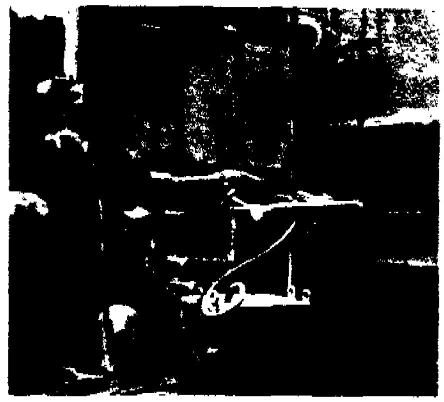
6. Install a double blocking bleed on the inlet steam line to the steam tracing. Responsibility - Department Supervisor.

7. These identical measures are to be done on a similar unit and according to the same schedule.

CASE HISTORY NO. 796

Midnight Explosion and Fire

Description: An experiment in crystal growing involving 20 grams of II-VI compound consisted of slowly passing the compound sealed in a quartz tube through a graphite ring heated by an RF induction heater to about 1200°C. Two fans were positioned to control the heat distribution, and nitrogen gas was used as a blanket around the ring. Several hours after starting this normally automatic operation, which had been unattended for about six hours, a mild explosion occurred, scattering the compound, broken quartz, and the graphite over the methyl methacrylate side and stone floor of the hood. The fans continued to run, as did the RF heater, and some time elapsed before a member of the night cleaning crew discovered the exact location, called in the alarm to an emergency phone, and returned with extinguishers to fight the fire. By this time the fire was rapidly spreading up the hood side and flames were creeping up the outside of the hood, catching a wooden trough which extended across the room. After unsuccessfully using two 2-1/2 lb. CO_2 extinguishers, about half of a 30 lb. dry chemical successfully extinguished the fire before the community fire department arrived. Due to prompt and rapid action, damage was confined to the apparatus and hood.



Preventive Measures: To minimize the effects of future incidents of this type, it is suggested:

1. All experiments intended to be left unattended overnight be logged in by the control center, so the patrol and other night personnel will have specific knowledge.

2. All combustibles and corrosives, such as bottles of solvents and reagents, be removed from hoods to preclude more serious fire spread or danger to fire-fighting personnel (a glass bottle of toluene and a plastic bottle of HF narrowly escaped rupture in this incident.)

3. Transite be used instead of plastics for hood shields wherever heat may be involved.

4. A fail-safe electrical hook-up be installed to cut off the fans and RF heater in case of fire.

5. The experiment be as adequately shielded on all sides as possible.

CASE HISTORY NO. 797

Operator Burned When Hose Connection Breaks

Description: An operator had been assigned the job of cleaning out the #2 Dehydrator system. He had completed the removal of the liquors in the system with the steam ejector and started the washes. When the first wash was completed, he requested the hook-up of a rubber steam hose from the discharge side of the #2 Dehydrator transfer pump to the storage tub which is used to store make-up water for the absorbers. (A steam hose had been used twice before for this job.) A department mechanic made the hook-up and also checked for leaks after the hose was in use. The operator stayed on the job until 12:00 noon when he left the plant for personal reasons.

Another employee, who was an extra operator that day, was assigned to the job just before going to lunch. When he returned at 12:15, the chief operator gave him the line-up and also told him to check the hose connection to the discharge pump. He went up to the 12 foot level where the hose was connected and observed that the hose connection to the piping on the discharge side of the pump was leaking badly. The spray from the leak prevented him from closing the valve to the hose. He then went directly to the switch for the transfer pump and turned it off. He started back to check the leak again when the connection gave way and allowed the hose to drop to the floor. The hot solution continued to spray out due to the static head pressure of the liquid in the system. He was approximately 10 feet from the connection when the injury resulted. Instead of using the shower on the 12 foot level, he immediately ran down to the ground floor where several operators assisted him to a shower and helped him remove his clothing. Before he was taken to the dispensary by the guards, he reported that the first shower he tried did not work. The shower was checked and found to be in good working condition. It is assumed due to the injured's excitement, he did not operate the shower correctly.

Cause: In the manufacturing of maleic anhydride, a section of the process requires the dehydration of maleic acid. The equipment used in this dehydration is cleaned out periodically. The exact time of the cleanout is dependent on a build-up of deposit of tars and residues which cause partial blockages and affect the vacuum. When a designated loss of vacuum is observed at the flash chamber, it means the equipment must be cleaned out. The first step in cleaning out the system is to suck all liquor in the system to the stripping still. After this is completed, water is introduced to the system and heated. A large circulating pump is started and the hot water is continuously pumped through the whole system for a half hour.

In the past, three separate washes were made on the system and on the completion of each, the liquor was pumped to the sewer. Through recent investigation, it was found that the first of the three washes contained maleic acid, so in an effort to better the yield, the liquor from the first wash is pumped through a rubber hose to the make-up water tank for the absorbers rather than being sewered. The second and third washes are still pumped to the sewer. A project was submitted and approved recently which includes the installation of a storage tank for this liquor and the permanent piping necessary to pump the first wash to this storage tub. The project is scheduled for the near future.

The committee feels that the rapid corrosion of iron fittings caused by maleic acid was the principal cause of this accident. The committee found that there were iron fittings on the steam hose and the piping to the pump. The installation of hoses with 316 s.s. fittings and 316 s.s. pipe fittings should prevent a recurrence of this type of accident. It would also provide a safer hose for unblocking lines in the department where it is possible that any of the material might come into contact with the hose fitting.

Preventive Measures: General: That each department supervisor will check hoses and fittings in his department from a corrosion standpoint. If it is found that the standard hose with steel or brass fitting is not suitable in all cases, it will be the production supervisor's responsibility for the following:

a. To determine what material is suitable in each case.
b. To see that material required is installed.
c. To acquaint operators with resulting changes.

Maintenance supervisors will assist production in the acquisition and installation of special materials.

Departmental:

1. That the following number of hoses with 316 s.s. fitting be provided for Department 49.
   1st level - one 50 foot hose
   12 foot level - one 50 foot hose (a 100 foot hose is on schedule for delivery)

24 foot level - two 50 foot hoses.
34 foot level - two 50 foot hoses.

2. That the hoses with 316 s.s. fittings be properly identified. The General Superintendent will determine method of identification.

3. That all blow-out and drain lines be changed to 316 s.s.

4. That supervision will inform personnel on location and use of special hoses.

5. That supervision will have signs reading, "Install hoses with 316 s.s. fittings only," installed at each steam water mixer when stainless steel fitted hoses are attached.

CASE HISTORY NO. 798

Safety Control Switch Not Permitted to Operate

Description: Employee was operating a preformer press which was actuated by a two-hand (two button) safety control switch on which he had jammed a match stick into the right hand button to hold it in the "on" position. As he attempted to clean the top of the mold while the press was closing, his right hand was caught by the ram seating with the mold.

Cause: Unsafe act of employee who had bypassed the safety controls by jamming a match stick in one of the start buttons in violation of the established safety rules and his supervisor's instructions.

Preventive Measures:

1. Time relay switches will be installed on the safety buttons so they cannot be operated if jammed.

2. A job safety analysis will be made of this operation.

3. A written warning was issued to the employee by his department head stating that any future violation of job safety instructions would result in severe disciplinary measures.

CASE HISTORY NO. 799

Perchloric Acid Explosions in Exhaust Blowers

Description: A maintenance worker was killed and two others were injured (one seriously), when an exhaust blower connected to a laboratory hood exploded. In September 1960, a similar explosion occurred at another uranium mill and a worker suffered painful injuries. In the summer of 1959, during the course of a casual inspection of a blower at another laboratory, an explosion occurred and the chief chemist suffered injuries to his face and eyes. Following this incident, and during the course of shop maintenance on four other blowers from the laboratory, four more explosions occurred, but there were no injuries since trouble was expected and safety shields had been set up to protect personnel.

Cause:

1. All of the blowers which have exploded have been used to exhaust laboratory hoods and the explosions are believed to be due to the formation of explosive compounds formed from reactions between perchloric acid fumes and a litharge-glycerine cement. However, other reactions involving laboratory reagent fumes may be contributory.

2. All of the blowers involved in explosions are made of a very hard and brittle corrosion resistant cast iron alloy which shatters into sharp angular fragments. In each case, the explosions have occurred while an attempt was being made to probe or remove the grouting cement which seals the rear face plates to the blower housing. On this particular blower, the manufacturer reports that the cement is composed of litharge and glycerine and it appears that this cement undergoes some reaction with perchloric acid fumes to form an explosive compound which is highly pressure sensitive. Explosions have occurred while lightly probing the cement with a screwdriver, while attempting to chip it out with a cold chisel, and during the course of removing it by sand blasting. Consequently, if you are using this type of blower for exhausting perchloric acid fumes, we believe that there is very nearly a 100% probability that an explosion will occur when an attempt is made to remove the cement grout on the rear face plate.

Preventive Measures:

1. The manufacturer now recommends that if this model fan is used in perchloric acid service that the glycerine-litharge cement be removed and that the plate be sealed with an inert cement. The following mixture is suggested:

   92 ounces - silica flour
   1/4 ounce - sodium fluosilicate (accelerator)
   Sodium silicate (water glass) sufficient to make a stiff paste.

2. The intensities of the explosions have varied. Some were very slight and involved no physical damage, while others were of such violence that they completely shattered the blower and propelled fragments for several hundred feet.

3. We have not been aware of any explosions with fans in which the face plate is caulked with asbestos rope and held in place by a steel retaining ring and dog clamps nor have we heard of explosions with other makes of fans or blowers. However, since it is well known that perchloric acid reacts with organic bearing materials to form explosive compounds, it is recommended that you make a careful examination of your laboratory hood exhaust system for the presence of wood or other organic construction materials such as rubber, plastics, and various sealing compounds. The use of corrosion resistant or ether paints on the interiors of blower housings and ducts should also be regarded with suspicion. If any are present it would be advisable to remove such materials, but such removal should be done only after setting up adequate safeguards to protect personnel.

4. Hosing down of ductwork and blowers at weekly or more frequent intervals is common practice at many laboratories, but is not a guarantee against this particular hazard. This is standard practice at the ---- laboratory, but an explosion occurred even after soaking the blower in soda ash solution.

5. Although we know of no instances of spontaneous explosions, this must be regarded as a distinct possibility. Safety measures should be employed when moving blowers and, in particular, personnel assigned to servicing of these blowers should be cautioned about inadvertently striking the face plate or sealing compound with a tool or grease gun. It is suggested each blower be conspicuously stenciled or tagged to indicate this hazard.

6. To guard against injury to personnel who must remove the face plates, the following setup has been divised: "The equipment is removed to a safe area and a steel shield erected and fastened to the fan housing. The nozzle on a sandblaster is rigged on a crank inside the shield and all the sealer removed by sandblasting. This method not only protects the mechanic from shrapnel and flying grout in case of an explosion, but also eliminates the possibility of injury to his hands from holding a chisel or other tool that he may use to remove the sealer."

United States Atomic Energy Commission

CASE HISTORY NO. 800

Explosion in Laboratory Propellant Cure Oven

Description: Specimens of experimental composite propellants were being cured in a steam-heated oven, located in a laboratory cell, when ignition occurred. The oven contained about 32 pounds of ammonium perchlorate propellant in open sample pans, and 70 grams of polynitramine propellant in 35 gram specimens, each in an aluminum weighing dish. One of these dishes was unconfined, the other was in a Parr combustion bomb under 60 psig pressure. Cure-temperature was 170°F. After 54 hours of curing, at constant temperature, sufficient pressure developed in the bomb to shear the head retaining ring. About 50% of the propellant burned. The top of the oven was blown off and the oven doors were blown open. The Parr bomb head and its retaining ring were found embedded in the oven top. The nitramine binder contained one ingredient, nitrated alcohol Petrin, which requires stabilization against decomposition – typical of nitrate esters. A commonly-used stabilizer, ethyl centralite, was employed for this purpose. Previously, the pressure cure of similar formulations had been performed apart from other propellants in cure. The success of these earlier experiments prompted the use of the Parr bomb for curing small specimens concurrently with other propellants.

Cause: Decomposition of propellant under pressure cure.

Preventive Measures: A complete autoignition profile is being obtained on this and similar propellants. Modifications to the pressure cure process will be considered, including use of low pressure relief diaphragms and the return to separate cure ovens or appropriate heated vessels.

Armed Services Explosives Safety Board

CASE HISTORY NO. 801

Drowned In Perlite

Description: On the day after an oxygen unit had been shut down for repairs to the main condenser, several employees were in a conical section of the housing to replace a blown rupture disc and to install a wood chute to remove perlite insulation prior to repair of the condenser. Some perlite (fine granular powder) flooded into the conical section suddenly through one or more of the four relief ports in the floor. The attendant dust cloud made vision practically impossible in the section. All employees got out of the area except one who was found about ten minutes later by a supervisor who had entered the area immediately to search for any trapped employees. Resuscitation efforts failed to revive the employee who had apparently inhaled quantities of perlite.

Cause: It is believed that the perlite flooding was caused by a sudden movement of a mass of the material in the upper section of the tower where ice formation had caused bridging which released the material when thawing occurred. The situation resulting in ice formation had been created by a leak in the main condenser.

Preventive Measures: Plans and design changes are being formulated to eliminate the hazard of flooding perlite into an area occupied by employees.

CASE HISTORY NO. 802

Fatal Exposure to Hydrogen Sulfide

Description: A synthetic chemical plant employee received an acute-fatal exposure to hydrogen sulfide gas while making benzimidazolethiol.

In this reaction ethylxanthic acid potassium salt is added to orthophenylaminediamine in alcohol. After the first reaction and refluxing, the mixture is acidified by adding glacial acetic acid. Large amounts of hydrogen sulfide may be given off during this acidification. The formulation procedure indicates that acetic acid is to be added slowly and that hydrogen sulfide must not be allowed to escape.

Cause: Evidence indicates that acetic acid was being added to the kettle by pouring directly from a plastic carboy without using a dropping funnel or other method of control. Evidence also indicates that the agitator was not running and that the vent ejector was not turned on.

A violent foaming apparently caused the material to froth out of the manhole, releasing a large amount of hydrogen sulfide. The frothing was sufficient to project some of the material from the mezzanine level to the first floor of the building so that other employees were immediately aware of the situation. The injured man was immediately removed and given rescue breathing with administration of oxygen but failed to revive.

The accident again demonstrates the high hazard of hydrogen sulfide and the need of every precaution to prevent release of material or inhalation of the gas. The area is equipped with air supplied respiratory equipment. The mixing kettle is provided with a dropping funnel to provide slow feed of acetic acid through a closed tube. The mixer is also provided with a vapor ejector and with an agitator.

CASE HISTORY NO. 803

Flash Fire

Description: Mixing operator had completed loading first part (425 gallons) of a batch of primer surfacer in the thousand gallon mixer. Among the last items loaded were four drums of nitrocellulose and two drums of gum. A flash fire occurred while he was cleaning the neck of the loading chute with a wooden-handled, bristle-type brush wet with a flammable solvent while the chute was still in the mixer manhole. The flash ignited the vapor above the liquid level in the mixer. The searing flame erupting from the manhole burned the employee on the face, neck, and shoulders before he was propelled from the mixer by the force of the explosion. Fortunately, he was wearing safety glasses which protected his eyes.

Cause: Specific cause of flash fire is not known. However, the use of a solvent wet brush for cleaning the residue from the loading chute was not standard practice and may have contributed to the development of a static spark which ignited the vapors in the mixer.

Preventive Measures: The clean-up procedure during loading is being reviewed, and standards are being raised, including minimum of clean up until mixer manhole is covered. The necessary brushing of the sloping sides of the brass loading chute (never the neck) will be done with water wet brush which does not have wire wrapping.

CASE HISTORY NO. 804

Rupture of Glass-Enclosed Magnetic Stirring Bar

Description: A commonly used laboratory stirrer is a small cylindrical Alnico magnet encased in an inert material such as glass or Teflon. The magnet is dropped into the fluid to be stirred and the vessel set on top of a magnetically linked motor which rotates a magnetic field and causes the stirring bar to rotate. One of these stirring bars, about 1-1/8 inches in length and about 3/8 inch in diameter encased with Pyrex glass, was the source of a possible personal injury to a laboratory assistant.

The accident occurred when the laboratory assistant took the stirring bar from the laboratory bench drawer and laid it on the bench top while he prepared a solution to be stirred. While the bar rested on the bench top, it suddenly ruptured with a loud report. The glass cover on the magnet broke into several pieces, one of which struck the arm of the laboratory assistant. Fortunately, he was not injured. An examination of the bar revealed that it was covered with scale and light-colored powder material. The powder had not been observed through the glass because of the presence of glass wool which apparently is used to cover the magnet before encasing it in glass. Laboratory tests show that the light-colored powder was iron sulfate. A small amount of black scale appeared to be iron sulfide.

Cause: The stirrer had been used on many occasions to mix solutions containing sulfuric acid. The glass seal must have contained a small pinhole due to improper sealing in manufacture. Over a period of time, sulfuric acid must have seeped into the glass case and formed the solid sulfate. The solid material must have built up to the point where the glass was ruptured.

Preventive Measures: In the future, only Teflon covered magnetic stirring bars will be used. The Teflon material is chemically resistant and is also flexible and would not rupture as did the Pyrex glass.

CASE HISTORY NO. 805

Flicked Acetic Anhydride Into Eye

Description: While preparing to siphon acetic anhydride from a drum by means of glass and rubber tubing a drip of anhydride flicked from the end of the flexible rubber tube and entered the operator's left eye. After treatment in the surgery he was examined by an eye specialist and detained in a hospital.

The siphon device consisted of a rubber bung bored for two glass tubes carrying lengths of 1/2-inch rubber tube approx. 2 ft.-6-in and 6 ft. long. The usual place of stowage was the flat top of a disused centrifuge 4 ft.-6-in. high on which the rubber tube was bundled haphazardly. It was obvious that any drainings which collected inside the tube between transfers would remain there until next time the tube was handled. No precautions were taken to guard against splashing from such drips apart from wearing of gloves and the general instruction that goggles must be worn during transfer of acetic anhydride. It appears that in the operator's interpretation of the instruction, the term "transfer" did not include "preparation for transfer."

It was noted that the usual method of starting the siphon was by application of a "touch" of works compressed air. Although this practice had no relevance to the accident, the committee nevertheless strongly deprecated the indiscriminate application of compressed air to drums.

Cause:

1. Unsafe procedure.
2. Failure to wear chemical goggles while handling corrosive material.

Preventive Measures:

1. A suitable stowage to be provided for the siphon device whereby the rubber tubes could hang vertically and drain into a suitable container.
2. Instructions on wearing of eye protection to be re-drafted and explained to all operators.

CASE HISTORY NO. 806

Tagging Not Enough

Description: The employee was reconnecting the piping to an anhydrous ammonia pump. While reaching over the equipment, he inadvertently bumped or leaned against a quick opening valve handle moving it to the open position. Anhydrous ammonia under 125 psi pressure was released through an open one-inch pipe ell onto the lower portion of his body resulting in severe burns to the lower torso and legs.

Note: This valve was red tagged and constituted the block valve in one of the suction lines that had already been connected to the pump.

Cause:

1. Limited work area.
2. The handle was not removed from the quick opening valve while work was being done near it.
3. The employee did not use good judgment in positioning himself for the work.
4. Employee reached over the equipment.
5. Possibility of laxity on the part of supervision in over-seeing the job.

Preventive Measures:

1. Valves of this type will have lever handles removed while such valves are red tagged.
2. Consideration is being given to replacing the lever handle with a wheel.
3. Additional emphasis will be placed on the need for prompt and adequate washing of

all external parts contacted by hazardous liquids.

CASE HISTORY NO. 807

Eye Injured--Pressurized Heat Exchanger to Locate Leaking Tube

Description: A fuel oil heat exchanger was allowing condensate to mix with oil, indicating tube leakage. Upon visual inspection of tubes, one tube was found plugged. A heavy wire was run through the tube until a light could be seen at the other end. The steam valve was then cracked to see if any steam was getting into the tube. An employee bent over to look into the tube and just at the instant his eye was level with the tube, the obstruction broke loose from the tube allowing oil and steam to hit him directly in the eye. He sustained severe thermal burns to his entire left eye.

Cause: Looking into the tube sheet with pressure on the equipment. Failure to wear face or eye protection when looking into a pressurized piece of equipment.

Preventive Measures:

1. The value of wearing eye protection at all times was stressed at the safety meeting.
2. Better methods of inspection are under consideration when performing maintenance work on tube and shell equipment.
3. A closer check on the department personnel and visitors in the wearing of proper eye protection is being made.

CASE HISTORY NO. 808

Inhaled Chlorine Gas

Description: A "chemical solution 2nd helper" on his first shift by himself, was checking the scale tanks. At this same time, he was making bleach liquor with liquid chlorine from the scale tanks. During this latter operation, the pressure in both scale tanks dropped below normal. In order to build the pressure back to normal, the compressor was started. As the pressure built up in the scale tanks, the flow of liquid chlorine to the bleach-making chest increased, resulting in the bleach liquor becoming overchlorinated and a considerable amount of chlorine gas escaping to the atmosphere. The concentration of chlorine gas was heavy and the "chemical solution 2nd helper," with his small respirator on, inhaled chlorine gas. The "chemical solution 1st helper" who was operating the reactor realized what was wrong and immediately went out to the scale tanks and shut off the liquid chlorine to the bleach-making chest.

Immediately following the escape of chlorine gas, the "Decker operator" went in to the Machine Room and advised the machine tenders on #1 and #2 machines. At the same time the machine room foreman and shift supervisor, noticed the strong smell of chlorine gas and not knowing what was wrong, agreed to get personnel out of the machine room until the condition cleared up. The machine room foreman carried out this plan of action. Personnel remaining in this area were equipped with full face respirators which afforded adequate protection for this concentration of chlorine gas.

Shortly after the release of gas, a Viscosity Tester was on the stairway when he noticed a strong smell of chlorine gas. He went back up the stairway to the Control Lab to get a respirator. On the way he inhaled chlorine gas. When he arrived in the Control Lab, he put on a full face gas mask. A Sample Collector in the Control Lab also inhaled chlorine gas and put on a full face gas mask. Another workman in this area also put on a full face gas mask and suffered no discomfort. The "Chemical Solution 2nd helper," the "Viscosity Tester" and the "Sample Collector" reported to first aid and were treated for exposure to chlorine gas.

Cause: The "chemical solution 2nd helper," on shift by himself for the first time, had three things to watch at the same time and forgot one, namely, the control of liquid chlorine to the bleach-making chest.

The "chemical solution 2nd helper" was apparently in a gas concentration too strong for the small personal respirator. The Viscosity Tester did not have his small respirator on his person. The Sample Collector was apparently not familiar with the full face gas mask and had difficulty putting it on.

Preventive Measures: All personnel have been given the following instructions:

1. If for any reason the person making bleach liquor with liquid chlorine has to leave the bleach-making system unattended for any length of time, or to perform another job, he must first shut off the liquid chlorine at the bleach making chest.
2. All personnel have received further instructions on the care and use of respiratory equipment.
3. This incident was discussed at a machine room safety meeting immediately following the occurrence and it was agreed that all the full face gas masks would be removed from the floor and serviced by the Fire Patrolman.

This operating procedure and others will be checked and brought up to date and placed in operating manuals for every job involving chemical solutions.

All supervisors will make certain that personnel in their respective departments must be fully instructed on (a) care and use of respiratory equipment and (b) ruling regarding the wearing of respiratory equipment.

4. All new employees will be instructed in above before commencing work.

CASE HISTORY NO. 809

Eruption of Hot Caustic from Repulper Vat

Description: The cook pump feeder on a washer repulper started to come loose and hooked on the cook pump impeller. Shear pins in a coupling sheared and stopped the pump. The drive motor and reduction gear continued to operate and the chute filled up. The level of stock came up into the repulper vat causing the repulper to kick out. The washer was shut off and the repulper was already immobilized. The supervisor asked if steam had been shut off but did not say whether he meant No. 4 or No. 5 chute. As steam had been turned off on the No. 4 chute, he was advised the steam was off. Believing it could be safely unplugged, the workmen started toward their area to start unplugging. At this time, a rumbling noise was heard from inside the repulper. Three of the men turned and started to get out of the area, but one man was prevented by pipes and valves in the way. The fourth man, not hearing the warning, made no attempt to get out of the way. Immediately following this loud noise, hot caustic stock and steam erupted from the repulper vat.

Cause: Had the steam lines been turned off properly, this accident probably would have been prevented. It is believed the steam could have heated up the stock and built up enough pressure to blow the stock up through the repulper. It was found that pressure in the line between the cook pump and the refiner mixer could cause the cook pump to rotate backwards which could have contributed to the blowback.

Preventive Measures:

1. Control valves have been installed on the steam lines to No. 4 and No. 5 washer.
2. A plugging switch on the cook pump will ring a bell if the rotor stops.
3. A back-stop braking arrangement has been installed to stop the cook pump from rotating backwards.
4. Valve has been moved so that workmen will not be trapped.
5. Each man has been instructed on safe procedure and the procedure has been written into the bleachery log book.

Armed Services Explosives Safety Board

CASE HISTORY NO. 810

Steam Pipe + Wood + Time = Fire

Description: The nitric acid concentration operator saw flames on the roof and wall near the absorption tower. The operator shut down the two concentration towers and telephoned the Power House and the foreman. The Power House advised the fire brigade and supervision. Electricity on adjacent power lines was turned off, and the fire was extinguished with fire hoses. A guard remained in the building overnight. The fire was not considered to be out of control at any time.

Cause: It is thought that the fire was caused by 20 psig steam tracing on a water line to the waste acid absorption tower. The tower has not been used since 1958, so it is concluded that the steam valve was turned on by mistake.

Sections of wood from the area of the fire were tested for combustibility. The ease of ignition was about the same as dry wood which has not been exposed to nitric acid fumes.

Electrical wiring and insulation adjacent to the burned wood was inspected and found to be in good condition, so it could not have caused the fire.

Preventive Measures:

1. Disconnect all unused steam lines.
2. Reinspect all steam lines passing through wood or other combustibles to ensure that they are installed in the approved manner, i.e., with adequate clearance and properly supported.
3. Connect small hoses on each floor of the nitric acid concentration building to the filtered water line for use in fighting small fires. This will provide water at 80 psig rather than 40 psig raw water.

CASE HISTORY NO. 811

Oleum Spill--Improper Procedure

Description: At 3:00 p.m., a mechanic went to the Sulfonator-Neutralizer area in the phenol plant to repair a leak in the oleum transfer line from the acid plant. He signed in on the maintenance log with the operator and requested him to have the acid plant advised and the oleum valve closed and tagged at the acid plant. Then the mechanic went out to the oleum tanks to watch for the acid plant operator to go out and tag the valve. There is a distance of about 100 yards between the oleum tanks and the valve, but the valve area was clearly visible. The mechanic did not see anyone go out to the valve, so he went to the acid plant and asked the swing shift acid operator to close and tag the valve for repair work on the line. The acid operator and the mechanic together went to the valve. It is an overhead valve operated with a chain from the ground level. A tag was placed on the chain with operator's name, and the mechanic put an acid plant lock through both sides of the chain and gave the key back to the acid operator. The mechanic then proceeded to repair the line. At 4:30 p.m., the repair was not complete, so a second mechanic took over the job. The first mechanic told him the valve chain was tagged and locked out at the acid plant. The line was cut open. It soon became apparent that the job would require a much longer time than first expected. The repair was postponed until the next day, and the line was left open. A note was put in the head operator's log book in phenol that the job would be completed the next day. The mechanic noted on the maintenance log at the Sulfonator-Neutralizer area that the job was incomplete. He called the acid plant and asked them to note in their log book that oleum should not be pumped the next day because the line was not repaired.

The next morning, at about 8 a.m., the acid plant day shift head operator read the note concerning the line repair and was unsure whether repair had been completed. He called the phenol Sulfonator-Nautralizer operator who checked the line in the vicinity of his valves and told the acid head operator that as far as he knew the line was all right. He was busy with process difficulties due to a stuck neutralizer agitator at this time. He did not check the maintenance log which showed the job as incomplete. He did not know what the job on the oleum line was although he could tell work had been done there because a 12 x 12-foot canvas tarpaulin was suspended in the vicinity. He did not look up at the pipe line to the level of the pipe bridge where the line was open.

The acid head operator advised the acid A operator that the phenol Sulfonator-Neutralizer operator said the line was all right. He told the A operator to pump the oleum. The acid head operator then went to the personnel building to talk to the mechanic who was just coming in to work. He asked him the status of the work on the oleum line. The mechanic said the line was open and would not be completed for some time. About this time, the acid A operator removed the lock from the line, removed the "Do Not Operate" tag and proceeded to open the valve which started oleum moving to phenol plant. He walked back to the control room and immediately the Sulfonator-Neutralizer operator phoned to tell him to shut the oleum line off due to an oleum spill. The quantity of oleum spilled was estimated at 25 gallons. No one was injured.

Cause:

1. Failure to follow correctly the lockout and tagging procedure.
2. Failure to make proper use of the maintenance log.
3. Lack of a designated responsibility for the oleum transfer line.

Preventive Measures:

1. At the time of a shift change, operators, as part of the normal informational exchange, will check the maintenance log for possible work going on in that area.
2. All operators and maintenance people will be given a review of the proper maintenance log procedure. Consideration should be given to possibly including the procedure in an "A" Bulletin.
3. All operations and maintenance people will be given a review of the tagging and lockout procedure with special emphasis on (1) use of personal locks and (2) proper use of tag signatures (who signs, what he signs, and when and by whom may the tag be removed).
4. Establish responsibility for interdepartmental pipe lines. (The committee firmly believes this should be a single department's responsibility.)
5. The Committee recommends that, consistent with normal acid plant procedure, future work on this particular line be done only after the pumps have been locked out or the line blinded.

CASE HISTORY NO. 812

Dangerous Procedure--
Heated Oil with Open Flame

Description: For several years turbine wheels have been placed on the shaft by using a hot oil bath to expand the hub of the turbine wheels. No accident has been experienced by using this method but the potential was always present.

Cause: The oil used for the bath had a flash point of 400° and was heated for several hours by four torches (four welders). The bath temperature often exceeded the flash point because the flame was hard to regulate accurately. Fumes from the hot oil were unpleasant to personnel besides causing a fire hazard. As the wheels were removed from the bath oil,drippings on the floor created a slipping hazard. By the old method it was very dangerous for the machinist to measure the opening because it was necessary to reach across the hot oil and near the flame to reach the center of the wheel.

Preventive Measures: A new assembly (cast) has been fabricated in our shops which is well insulated and electrically heated. The heat can be raised to 600° without any danger of fire or hazard to personnel. Besides eliminating the various hazards, the job can be done with a fraction of the manhours formerly used. The degree of expansion can now be measured easily by simply removing a small section of the top insulation without any hazard to the machinist.

CASE HISTORY NO. 813

Sulfuric Acid Sprayed in Face

Description: A pair of pipers were removing a nipple and cap from a 66° Be. sulfuric acid line in preparation for installation of a valve. This section of line was between two closed valves and had not been used for approximately 20 days. One piper had gone for the valve while the other piper was unscrewing the nipple. At that time the production foreman came up to spread a little soda ash on the few drops of acid that had come from the loosened nipple. As the last thread was disengaged, acid spurted out of the line spraying both men about the face and neck. The piper was wearing splash goggles and the foreman had on safety glasses, thus preventing possible blindness to the two men.

Cause:

1. Reaction of the sulfuric acid on the iron line releasing hydrogen, thus building up pressure.
2. No provision for bleeding line prior to dismantling except back to storage or to reaction vessel (where another type batch was being made).
3. Insufficient knowledge that the acid could react and build up pressure.

Preventive Measures

1. Production supervision will each check their own areas to make sure they do not have acid in contact with iron in a completely closed system.
2. All plant personnel have been made aware of the fact that confined acid in iron can cause pressure build-up.
3. Emphasis to be placed on this incident by all supervision to further promote the use of safety eyewear in the plant.

CASE HISTORY NO. 814

Sheet-metal Worker Injured--Jumped from Ladder when Oil Pan Spilled

Description: An Engineering Department sheet-metal worker and co-worker were removing an oil drip pan located near the ceiling on the first floor. The pans are 70 x 90 inches, made of aluminum, and are secured to overhead beams with brackets. The pans are equipped with a drain pipe. They were attempting to drain the oil out of the pan by using the drain pipe. After removing about 1/2 gallon, the oil stopped flowing, and they were under the impression the drain line was stopped up and proceeded to remove the oil by removing the end bracket and tilting the pan down. While doing this, one side of the pan slipped out of the bracket and released a large quantity of oil. As he attempted to jump out of the way of the oil, the sheet-metal worker slipped and fell, fracturing his pelvis.

Cause: Unsafe Act: Unsafe work method—oil drain line was not stopped up as thought. A low place in the pan, due to the weight of the oil, had prevented the oil from flowing out of the drain pipe, located at the east end of the pan.

Employee apparently failed to recognize the amount of oil left in the pan and the weight factor, which obviously had not been taken into consideration in the design.

Preventive Measures: Supervisors must insure that employees realize the importance of appraising work situations prior to proceeding and must select work methods which will not result in accidents and personal injury. Not only must employees be well trained in safe practices, but they must be motivated to want to work safely.

CASE HISTORY NO. 815

Tank Truck Driver Burned with Acid--Working Alone

Description: An "outside" acid truck driver was splashed with 20° Baume hydrochloric acid about the face, eyes and chest. The accident occurred on top of the truck platform as the driver was disconnecting the hitch on the acid hose delivery line. At the time of the accident, the man was alone in the area of the unloading station. He made his own way, a distance of approximately 100 feet, and was placed under a safety shower by the employees.

Cause: The truck driver violated the plant rule that outside drivers neither connect nor disconnect to company storage tanks. The acid is unloaded from the tank truck by blowing with air. The driver disconnected the transfer hose before the air pressure had been completely vented. Although the transfer line valve was closed it was faulty, permitting residual acid to spray out when the hose was disconnected. The driver was not wearing goggles.

Preventive Measures:

1. The purchasing and traffic departments have notified the carrier to insist that their truck drivers observe the plant regulations.

2. The operating personnel in this area have been reinstructed that outside truck drivers are not to handle any of the unloading equipment.

3. This review is being circulated to plant supervision to show the hazards which result when "outside" truck drivers do not comply with plant regulations.

CASE HISTORY NO. 816

Vinyl Chloride Polymerization Explosion

Early in the morning, August, 1961, an explosion broke out at the Minamata Plant of the New Japan Nitrogen Fertilizer Co., claiming four lives and injuring ten people in or around its premises.

The plant is situated at Minamata, a city in the southwestern part of Kyushu, one of the four main islands of Japan. It occupies about 100 acres in which there are about 500 buildings accommodating manufacturing plants, warehouses, offices and many tanks. The total floor area of buildings is about 1,430,000 sq. ft. and the number of employees exceeds 3,500.

These buildings are principally of asbestos or stucco clad steel frame or stucco clad wooden frame construction, and some of them, including office buildings, are of wooden construction.

The plant produces varieties of chemical fertilizers and plastics including polyvinyl chloride, and the explosion occurred in the vinyl chloride polymerization plant, a building containing 18 pressure vessels, in which polyvinyl chloride is produced from vinyl chloride monomer under the pressure of 100 to 160 lb./in. at the temperature of 120 to 140 F. It takes between 10 and 15 hours to complete this polymerization in the pressure vessel. The characteristics of vinyl chloride monomer CH_2CHCl are as follows:

boiling point: $-13^{o}C.$ ($9^{o}F.$)
specific gravity: approximately 2
explosion range: between 4 and 22%

During the polymerization process, the vessel is cooled because heat is generated during the reaction. The temperature and pressure within the vessels are checked by the operators with gauges and meters in the controller's room. When the temperature has stabilized and the pressure has settled down, thus indicating completion of the reaction, they stop the churning of material, open the lid on the top of the vessel. They then open the discharge valve at the bottom through which the liquid products are transported through a manually operated funnel and pipe to the drying and crushing plant, adjoining the polymerization plant.

About half past 6 o'clock in the morning, as the reaction in the polymerizing vessel No. 3 was completed, a foreman and three employees set to work to discharge the contents according to directions from the controller's room but in error they opened vessel No. 4 instead of No. 3. Thus the gaseous vinyl chloride monomer just in the process of polymerization burst out of the vessel, filled the room and shortly afterwards exploded, presumably ignited by a spark from electric machines or by static electricity generated by the bursting gas, or some other unknown cause.

The explosion was heard at the municipal fire department about a mile distant from the factory. A fireman on the watchtower saw black smoke clouds rising from plant buildings, but he did not see any flame.

When firemen arrived at the scene, there were thick white smoke clouds with a smell of gas around the polymerization plant, and near vessel No. 4 a little flame was found. The fire was extinguished after a few minutes. Then they worked to rescue the wounded employees and stayed there for a possible secondary explosion, which fortunately did not occur.

The foreman was found dead at the top of No. 3 tank and one of the two workers at the bottom was dead on arrival at the hospital. An employee in the controller's room died instantly and another worker in the burner plant, a building next to the polymerization plant, died after two days. Within the premises of the factory, 8 additional persons were injured, most of them not seriously, and outside the factory two persons were injured slightly by flying glass.

All the asbestos plates on the roof and walls of the polymerization plant fell out, and parts of stucco walls were also blown down. Inside the building, the steel frame was dented or buckled by the shock of the explosion; iron floor plates in particular were seriously damaged, some of them cut off, others blown away. All the glass panes on the doors and the windows were blown off.

None of the 18 vessels were damaged seriously, with the exception of vessel No. 3 which was greatly dented on the side.

CASE HISTORY NO. 817

Sprayed with Hot Maleic Acid Solution

Description: An operator had been assigned the job of cleaning out a dehydrator system. He had completed the removal of the liquors in the system with the steam ejector and started the washes. When the first wash was completed, he requested the hook-up of a rubber steam hose from the discharge side of the dehydrator transfer pump to the storage tub which is used to store make-up water for the absorbers. (A steam hose had been used twice before for this job.) A department mechanic made the hook-up and also checked for leaks after the hose was in use. The operator stayed on the job until 12:00 noon when he left the plant. Another employee, who was an extra operator that day, was assigned to the job just before going to lunch. When he returned at 12:15, the chief operator gave him the line-up and also told him to check the hose connection to the discharge pump. He went up to the 12 ft. level where the hose was connected and observed that the hose connection to the piping on the discharge side of the pump was leaking badly. The spray from the leak prevented him from closing the valve to the hose. He then went directly to the switch for the transfer pump and turned it off. He started back to check the leak again when the connection gave way and allowed the hose to drop to the floor. The hot solution continued to spray out due to the static head pressure of the liquid in the system. He was approximately 10 ft. from the connection when the injury resulted. In the manufacturing of maleic anhydride, a section of the process requires the dehydration of maleic acid. The equipment used in this dehydration is cleaned out periodically. The exact time of the cleanout is dependent on a build-up of deposit of tars and residues which cause partial blockages and affect the vacuum. When a designated loss of vacuum is observed at the flash chamber, it means the equipment must be cleaned out. The first step in cleaning out the system is to suck all liquor in the system to the stripping still. After this is completed, water is introduced to the system and heated. A large circulating pump is started and the hot water is continuously pumped through the whole system for a half hour. In the past, three separate washes were made on the system and on the completion of each, the liquor was pumped to the sewer. Through recent investigation, it was found that the first of the three washes contained maleic acid, so in an effort to better the yield, the liquor from the first wash is pumped through a rubber hose to the make-up water tank for the absorbers rather than being sewered. The second and third washes are still pumped to the sewer. A project recently was submitted, approved and is scheduled for the near future which includes the installation of a storage tank for this liquor and the permanent piping necessary to pump the first wash to this storage tub.

Cause: It is believed that rapid corrosion of iron fittings caused by maleic acid was the principal cause of this accident. It was found that there were iron fittings on the steam hose and the piping to the pump.

Preventive Measures:

1. Hoses used for this operation to be provided with 316 stainless steel fittings, and these hoses properly identified.
2. All blow-out and drain lines to be changed to 316 stainless steel.
3. Inform personnel on location and use of special hoses and post sign INSTALL HOSES WITH 316 S.S. FITTING ONLY at each steam water mixer when stainless steel fitted hoses are attached.
4. Each department supervisor check hoses and fittings in his department from a corrosion standpoint. If it is found that the standard hose with steel or brass fitting is not suitable in all cases, production supervisor should: determine what material is suitable in each case, see that material required is installed, acquaint operators with resulting changes.

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CASE HISTORY NO. 818

Hydrogen Sulfide Release--Near Miss

Description: The operator and his supervisor went to investigate an H_2S odor coming from a reduction vessel. The fumes were so pungent the men experienced difficulty in breathing and immediately headed for an exit. When they got outside the operator collapsed but revived quickly and was taken to Plant Health.

Cause: The scrubber unit to which this vessel was attached, had been charged with fresh solution before the reaction began. The scrubber blower, which is interconnected with an alarm, is shut during this procedure and the alarm turned off manually. After the scrubber was returned to service, the alarm bell was not turned on. During the reduction step, the blower motor failed mechanically but since the alarm was shut off, the operator was not aware of the failure. The H_2S fumes escaped into the room creating the noxious situation.

The operator was attending a vessel in another part of the room and was not aware that the H_2S was escaping. This gas has the insidious property of causing olefactory fatigue and dangerous concentrations cannot be smelled after short exposure.

Preventive Measures: To prevent a recurrence, the batch sheet was revised to require the operator's signature that the alarm has been re-energized. In addition, it has been found that a lead acetate solution will absorb H_2S and detect it in the HCN detector in this room. This will ring an alarm when H_2S escapes into the room. Lead acetate paper also is available to be used when leaks are suspected.

CASE HISTORY NO. 819

Aluminum Triethyl Fire

Description: A chemist dropped a gallon glass bottle containing about two liters of a 20 per cent solution of aluminum triethyl in kerosene when his feet slipped on slick mud on the walk at the entrance of a sample storage shed. The released solution flashed on contact with air and moisture, enveloping the chemist who had fallen to a sitting position. A plant safety inspector, fully dressed in protective clothing, mask, and gloves who was present to destroy discarded samples, immediately pulled the chemist to a dry area and extinguished his burning clothing. The safety inspector secured help from the adjacent laboratory and carried the chemist inside to a safety shower where clothing was removed and showering was continued for fifteen minutes under supervision of the plant nurse. The nurse also gave him a pain-killer. The local hospital was alerted and a team of doctors was waiting for the patient upon his arrival in the plant ambulance. They found the injured man to have second and third degree burns on both hands and forearms, second or third degree burns on both buttocks, and first degree burns of the face. Treatment was spectacularly successful, with release from the hospital in 17 days with prognosis of no permanent disfigurement and no necessity for skin grafting. The injured man returned to work with no limitations on the thirty-third day.

Cause:

1. Detailed safe-handling rules for aluminum triethyl had not been issued for laboratory workers, although such rules were in effect in the plant.
2. The chemist wore no protective clothing, mask or gloves while handling the comparatively large container of aluminum triethyl.
3. The glass container was carried in the hand rather than being cushioned in an inert absorbent material in a bucket.

Preventive Measures:

1. Glass bottles containing more than eight ounces of aluminum triethyl solution will be carried only in a bucket cushioned with vermiculite or other inert material.
2. Approved protective clothing will be mandatory for anyone handling amounts of aluminum triethyl solution exceeding eight ounces.
3. Proper grading of the area will be done to prevent rain-washed mud from coating the concrete walk between the laboratory and sample storage house.
4. Detailed safety rules have been promulgated covering aluminum triethyl handling in the laboratory.

CASE HISTORY NO. 820

Blast Effect Injury

Description: A solution of 195 gm. of dibromomalononitrile in 600 ml. of ethyl ether was added to a solution of 197.5 gm. of sodium azide in 600 ml. of water (mechanical stirring) over a period of 45 min., while maintaining the temperature of the reaction at 5-8°C. by means of an ice-bath. After the addition was complete, the reaction mixture was stirred for an additional 2 hrs. at 10°C. The ether layer was then separated and discarded. The aqueous layer was extracted six times with 500 ml. portions of ether and these extracts discarded. The water solution was then acidified with 175 ml. of a 1:1 mixture of concentrated H_2SO_4 in water. An oily product separated out which was taken up in 500 ml. of ether. The water was extracted once with an additional 500 ml. of ether and the water discarded. The ether extracts were combined and dried over anhydrous sodium sulfate. After filtering off the drying agent, the product solution was poured into a large evaporating dish in a hood late in the afternoon. The next morning the chemist stirred the oily product left in the dish and at about 10:00 a.m. noted that some crystals had started to form. Several times later in the day, the chemist stirred the slurry with a metal spatula in order to induce more crystallization.

At about 4:05 p.m., the laboratory technician reached into the hood to adjust a rack. He did so without touching or otherwise disturbing the evaporating dish. Just as he withdrew his arm, the slurry in the evaporating dish (estimated to be 75-100 gm.) exploded with great violence breaking bottles containing solvents and sodium stored in the hood. The technician's shirt and safety glasses were blown off and he sustained multiple abrasions (blast effect) of chest and both arms, multiple puncture wounds of the chest, abdomen and right arm, ruptured right ear drum and scratch on right eye.

The reaction between dibromomalononitrile and sodium azide had been run previously using 1/5 the quantities used in the run which exploded. The products of these runs when isolated as an oil suspension of crystals did not explode when struck with a hammer on a steel plate. The material would decompose rapidly when heated in a flame. Pure crystals of the product isolated by dissolution in ether followed by reprecipitation by the addition of chloroform were very shock-sensitive when dry.

Cause: The amount of material being handled was grossly in excess of that considered safe to be used in a laboratory hood. Even if shielding, remote handling devices and ear protection had been employed, it is probable that a serious injury would have been sustained. The fact that two of the four frontal hood shields were in the open position probably permitted the explosive force to be dissipated and resulted in lesser initial damage and less serious injury than would have occurred had all shields been lowered.

Preventive Measures: A maximum of 2 grams will be handled during any future reaction.

CASE HISTORY NO. 821

Firebox Explosion--Dowtherm Vaporizer

Description: At approximately 8:40 a.m. instruments in the control room indicated a flame failure of the Dowtherm vaporizer, F-5. Operating personnel immediately checked F-5 and found it was not operating. According to furnace start-up procedure, the firebox was checked before activating the control unit which automatically purges and lights the furnace. After the purge cycle, when the pilot ignited, there was a firebox explosion at 8:50 a.m. Extensive boiler casing and refractory damage resulted from the explosion. No other equipment or buildings were damaged. These events occurred several hours after a severe rain and electrical storm.

Cause: A short developed across the fuel selector switch which allowed the fuel gas valve to open during the purge cycle, thus purging the furnace with a mixture of fuel gas and air. When the pilot ignited, the explosion occurred.

There were no personnel injuries as a result of the explosion.

Preventive Measures: The fuel selector switch has been removed from the control circuit and all exposed connections have been weather-proofed. Consideration is being given to the installation of a roof over the front end of the boiler; the use of a continuous pilot flame and isolation of wiring circuits to reduce probability of "shorting." Damage was estimated at $15,000.

CASE HISTORY NO. 822

Ether Explosion in Laboratory

Description: A chemist was distilling ether from impurities when an explosion occurred, resulting in burns of the face, hand, arm and leg. The apparatus consisted of a distillation flask, coupled with a water-cooled condenser draining the ether into a three liter bottle. The source of heat was a single steam bath. The hood contained some extraneous equipment of which there was a thermostatically-controlled hot plate with exposed contacts. The distillation was being carried on when the chemist added more ether to the flask. A bump caused by the steam raised the flask slightly. The chemist stepped over next to the hood to cut the steam back, and at that moment, the explosion occurred. The explosion caused the explosion-venting windows to open, but the venetian blinds were broken.

Cause: The connection between the flask and the condenser broke, permitting ether vapors to fill the hood faster than they could be removed. The vapors were ignited by the hot plate.

Preventive Measures:

1. Sources of ignition should be removed from areas where flammable liquids can escape. Hot plates, open flames, unapproved electrical equipment, etc. are included in this category.
2. Laboratories should be designed so that it is not possible for persons to be trapped by fire.
3. Explosion venting windows should not be obstructed. Venetian blinds offer considerable resistance to explosion pressures.
4. Consider the hazards of a job and then choose the suitable conditions to carry it out.
5. Discuss new arrangements or procedures with the safety leader. His experience is valuable in recommending safe procedures.

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CASE HISTORY NO. 823

Benzene Laboratory Fatality

Description: A chemist was placing a twelve liter 3-necked flask nearly full of benzene on a cork ring located on a hooded laboratory bench. Another chemist and a technician were in the immediate vicinity. The flask broke about twenty degrees up from the bottom and the benzene spilled onto the bench, floor, and to varying degrees on the clothing of the three men. In the ensuing moments three electric plugs located below the level of the bench were disconnected, terminating electricity to a hot plate located under the hood, to an agitator motor, and to a motor driving a vacuum pump. The plugs and sockets were of the standard two-prong variety. The benzene ignited, setting fire to the clothing of one chemist, the technician, and to a minor degree that of the second chemist. All three men rushed outdoors from the laboratory where they were wrapped in blankets and subsequently taken to a nearby hospital. The technician died of extensive third degree burns, one chemist was severely burned but survived, and the third man was only slightly burned. A safety shower within four feet of the accident was not used because of heavy smoke and panic.

Cause:

1. The flask may have been damaged or defective, causing the rupture.
2. Pulling out the electric plugs probably caused a spark which ignited the benzene.

Preventive Measures:

1. All flasks will be meticulously inspected in the future.
2. In the event of spillage of flammable solvent, the immediate and adjacent areas will be cleared of all personnel. After evacuation is complete, the outside main electrical switch will be thrown to terminate service to the contaminated and adjacent areas.
3. All electric plugs in the laboratory have been changed to the three-prong variety, a type that cannot be pulled out before unscrewing.
4. Since three-necked flasks are structurally weaker than those with fewer necks, the volume of flammable liquids used in three-necked flasks should be kept to an absolute minimum.

CASE HISTORY NO. 824

Liquid Oxygen Explosion

Description: An explosion occurred at the liquid oxygen filter near the storage tanks at a static test stand. The liquid gases unit of the propellant handling section was requested by the static test stand to pump liquid oxygen to the missile booster. At 11:15 a.m. the foreman placed one crew of men on the 28,000-gallon tanks and another crew consisting of 3 men on the 14,000-gallon tanks. Precooling of the 6-inch line from the 28,000-gallon tanks and precooling of the 4-inch line and filter from the 14,000-gallon tanks was started at 11:30 a.m. At 11:40, the tower notified the crews that the liquid oxygen pumps should be started. The crew on the 14,000-gallon tanks noticed that there was no power to the pumps and notified the foreman, who went to the tower and located an electrician who threw a main breaker which connected power to the pumps. In the meantime, the pumps at the 28,000-gallon tanks were primed and pumping. At 11:50 noon the 250 gpm liquid oxygen pump at Tank No. 2 was started and put on the line. At 12:00 a.m. the foreman went to the 500 gpm liquid oxygen filter of the 14,000-gallon tanks and noted that the pressure drop across the filter was approximately 2 psi. The pump discharge pressure was 175 psig. At 12:05, the foreman reviewed overall conditions at both tanks and went to the static test stand. The 3 crewmen at the 14,000-gallon tanks were positioned at the end of the No. 1 Tank observing the pump discharge pressure and tank level gauge. At 12:10, without any warning, the 500 gpm liquid oxygen filter at the 14,000-gallon tank exploded. The shock wave from the explosion struck the concrete fire wall and knocked the 3 crewmen against the guardrail installed around the operating platform. Parts of the filter, and steel grating over the filter, were blown with considerable force over the entire area, up to distances of 450 feet. The ruptured liquid oxygen lines immediately covered the area with liquid oxygen vapors and at this point, the 3 crewmen ran from the tanks in the direction of the pillbox south of the tanks. The crew on the 28,000-gallon tanks also left their station, but shut down the pumps prior to departure. The pumps at the 14,000-gallon tanks being left in operation caused a very large spillage of liquid oxygen at that location. However, by 12:15, the foreman and the test stand personnel had called the fire department, sent the 3 crewmen to the hospital for medical check, thrown the 14,000-gallon pump breakers to shut down the pumps, and turned on the deluge sprinkler system at the 28,000-gallon tanks. The chief of the propellant handling section arrived at this time and directed the action to control the spillage hazard. By following behind the spray from the water hose used by the propellant crew at the tanks, he was able to clear a path through the heavy liquid oxygen vapor and close the liquid discharge valves and open the vent valves on the 14,000-gallon tanks. The foreman, in the meantime, secured the 28,000-gallon tanks in a similar manner. The fire department arrived at approximately 12:20, connected their water hose, and commenced to wash down the liquid oxygen spillage. By 12:45 the liquid oxygen vapors had been cleared from the area and the tower area was cleared for access. There were no injuries.

Cause: A detailed study of the damaged filter components indicated that the explosion could have resulted from one of the following conditions (listed in the order of most probable cause):

1. A filter element became loose and was vibrating in the aluminum header plate. A particle of contaminant was lodged between the element and header plate and was impact detonated causing subsequent burning of the aluminum header plate.

2. Contamination had built up on the filter element and a heavy foreign particle traveling at considerable velocity in the line struck the contaminant when it reached the filter element with sufficient impact to cause detonation and subsequent explosion.

Preventive Measures:

1. All liquid oxygen filters will be dismantled, inspected, cleaned, and elements and gaskets replaced with clean components every 2 months, unless for some reason the allowable pressure drop across filter reaches the maximum.

2. All liquid oxygen tanks will be chemically cleaned every 12 months in lieu of original schedule of 18 months.

3. All filter aluminum components will be replaced with stainless steel as soon as they become available.

4. Develop improved filter design (such as element threaded connections to prevent movement, etc.) and incorporate these design modifications at the earliest possible date.

5. All remotely located circuit breakers which control power to the propellant facilities will be clearly identified so that in the event of future accidents, responsible personnel can quickly disconnect all power to these facilities. As soon as all power to these facilities has been disconnected, notification of such will be given to emergency crews and other personnel who are required to enter the accident area.

6. Install remote controlled, pneumatic operated liquid oxygen tank discharge valves so that remote operation may be had in event of emergency.

CASE HISTORY NO. 825

Metallic Sodium Fire and Explosion

Description: At the start of a centrifuging operation outside of the building, a valve was left open causing organic material to run onto the cement slab. Before cleaning up the spill with water, a drum was disconnected from the centrifuge, and a bung was screwed into the opening. After a short time of washing the spill with water, a fire enveloped the area. The injured employee attempted to put out the fire with a CO_2 extinguisher while his co-workers went for help. The disconnected drum alongside the centrifuge exploded causing a flash fire which surrounded the injured employee. The injured employee received moderate burns to the hands and face. Pertinent facts of the incident prior to the explosion: 1) one step in this reaction is to add a metallic sodium dispersion into the reactor; 2) the reaction of all of the additions proceeded as planned throughout the day; 3) a sample of the reaction product was taken from the bottom of the reactor – part of the sample was thrown on the snow so that any unreacted metallic sodium would react with water – no reaction of any type was noted – the reaction mixture was also treated with acetone and no reaction occurred – it was then decided that there was no metallic sodium present; 4) as the wheeling operation was started, the bottom outlet of the reactor was opened (there was approximately 8-10 psig Argon on the reactor) – as this was done, it was determined that the valve to feed the centrifuge was open, which allowed material to flow to the wheel and onto the floor – while this was happening, the drum on the filtrate side of the centrifuge was connected and approximately 2-3 gallons ran into the drum; 5) the drum was disconnected from the centrifuge and a bung was screwed into the bung opening; 6) the operator using a service water hose washed the spilled material toward the sewer – all of a sudden, the spilled material was enveloped in flames.

Cause:

1. Metallic sodium was in the spilled material because of an incomplete reaction.

2. Water was used on metallic sodium because tests failed to show its presence.

3. The valving was not checked prior to the centrifuging operation.

4. The bunged drum in the area was heated by the fire resulting in an explosion.

Preventive Measures: 1. Develop a more adequate test and sampling procedure to determine the presence of a residual metallic sodium in the final product.

2. The drums used on the filtrate part of this job will be equipped with flame arresters. Containers of flammable materials will be removed from area before cleaning up a spill.

CASE HISTORY NO. 826

Chemical Burn--Know the Job

Description: The injured employee started to hook up a bromine trailer in preparation for unloading. Realizing he was new on the job and not being sure of the hook-up, he secured a co-worker to check his work. After the check, he removed the blank from the unloading line (dip pipe) without opening the vent to release the internal pressure in the trailer. When the blank was removed, bromine gushed out of the unloading line and sprayed on the left leg of his trousers. He received chemical burns to the lower left leg and the ends of three fingers of his left hand.

Cause: 1. Insufficient instruction - this was the first time the injured employee had done this operation. The co-worker he asked to check him, apparently did not know the correct procedure.

2. The operating procedure, including a check list, was not used on this job.

3. The pressure, which built up in the trailer by temperature change, was not vented before removing the blank on the dip pipe.

4. The employee failed to wear the proper personal protective clothing, which is prescribed by the operating instructions (he was wearing only side shield glasses and leather gloves).

Preventive Measures: 1. Supervisors will instruct employees of the necessity of asking questions if they are not sure of an operation. Employees will be instructed that there is no disgrace connected with not knowing all details about all jobs.

2. Supervisors will sharpen communications - to make sure personnel understand instructions and follow them.

3. Supervisors will emphasize the need for employees to help their co-workers before they are involved in an accident.

CASE HISTORY NO. 827

Insecure Charging Cap under Pressure Strikes Operator

Description: An operator was in the process of transferring a catalyst slurry batch to an autoclave by pressurizing the catalyst slurry tank with nitrogen pressure. When the pressure on the tank reached 15 psig as stated by the operator, he was struck on the right cheek by a 4-inch pipe cap used to close the catalyst charging port for pressurization of the vessel. The cap hit him a glancing blow opening a laceration in his right cheek requiring 12 stitches to close.

The operation of preparing and transferring a catalyst charge to the autoclave is as follows:

1. Addition of recycle catalyst to slurry tank.

2. Addition of some amount of biphenyl to make resultant slurry thin enough for transfer.

3. Charging of a weighed amount of catalyst by a 10-quart bucket to the slurry tank through a funnel inserted into a 4-inch nozzle on the tank.

4. Agitation and closure of 4-inch threaded nozzle with pipe cap.

5. Opening of two cocks in transfer line. One opened first at autoclave, second opened at slurry tank just prior to transfer.

6. Pressurization of slurry tank to 80 psig with nitrogen to transfer catalyst slurry through bottom outlet to autoclave.

The accident occurred during Step 6, and as stated by the injured, when he had observed the build-up of pressure to 15 psig.

Cause: Investigation by the Committee has shown that the primary cause for the accident was the continued use of the screwed charging nozzle and pipe cap for access to and closure of this vessel. The threads of both were found to be partially stripped and/or worn so that cross threading was likely to occur and had happened on some occasion. In addition, the transfer cock and nitrogen valve were so located that their operation required attention in front of the charging nozzle while pressure was being applied. Summarizing, the accident was caused by:

1. Equipment in poor repair.

2. Poor equipment lay-out.

Other unsafe conditions related to this operation were found during the course of the Committee's investigation. They are:

1. Pressurization of slurry tank above maximum allowable working pressure recommended by ASME. The plate head of this vessel has a calculated M.A.W.P. of 40 psig. Eighty psig pressure is required to transfer slurry.

2. Slurry tank has no pressure relief mechanism. Failure of two cocks, or improper operation could result in autoclave pressure (300 psig) being applied to this vessel.

3. Vent line, and valve on slurry tank too small for rapid release of pressure after transfer completion.

4. No pressure reduction station, or pressure relief mechanism other than that at nitrogen cylinder bank in nitrogen supply line. 200 psig could be applied without proper operator attention.

Preventive Measures: The following recommendations are made by the Committee:

Immediate:
1. Relocate nitrogen piping so pressure can be applied from safe location.
2. Install relief valve set at 80 psig in nitrogen supply line.
3. Increase nitrogen vent valve size.
4. Replace worn 4-inch pipe cap.

Future:
1. Upgrade spare catalyst slurry tank to adequate safety by:
   a) Repair of agitator shaft.
   b) Installation of two stiffeners to top head plate to increase M.A.W.P. to 200 psig.
   c) Install 150 psig rupture disc on catalyst slurry tank.
   d) Revise charging nozzle. Use Hamer line blind for tank closure.
2. Upgrade slurry tank now in use to above, or dismantle so that future use is impossible.

Plant Wide: All supervision to survey their departments where gas pressure is used for the agitation, or liquid transfer for similar hazards, and submit recommendations for their correction.

CASE HISTORY NO. 828

Acid Line Opened before Tank Car Was Vented

Description: An employee had been assigned to connect up and unload a tank car of 98% sulfuric acid. This job had been assigned to this employee for a number of years and he had been instructed in the proper procedure to follow when performing this function.

On this day, the employee failed to vent the pressure (created by the summer heat) from the dome of the car. When he removed the cap from the pump-out line, internal tank car pressure caused acid to spray out around the cap and onto his hands, arms and legs. The employee was able to wash the acid off quickly, thus averting a serious injury.

Cause: Failure to vent the tank car before opening the pump-out line was the cause of the accident.

Preventive Measures: The following steps have been taken to prevent a recurrence:

1. The injured employee was reprimanded and again re-instructed to use protective equipment and to follow correct unloading procedures.

2. All other employees who might perform this duty were warned and instructed to follow correct procedures.

3. An enclosure for protective equipment and new protective equipment has been secured and installed near the job site.

4. Correct procedures to follow are to be posted in the area in the proper order of job-steps to follow. These will be listed in sequence and will serve as a reminder to do the job correctly.

CASE HISTORY NO. 829

Hard Hat Barely Saves Life

Description: Two sets of chain falls were being used through a floor opening to place a length of six-inch pipe on the floor below. One set of falls was attached to building steel with a beam clamp. The other, however, was suspended from a piece of channel iron which had been wedged between two steel beams.

The channel iron, together with the chain falls, slipped and fell, striking a member of the plumbing department on the front of his safety hat. He received lacerations of the scalp and right ear, with a possible minor skull fracture. The safety hat was broken half way across the front.

Preventive Measures: Even though the safety hat is credited with preventing a serious, possibly fatal injury, the injury potential of this setup was extremely serious.

The accident indicates the necessity of arranging supports for every type of rigging in a thoroughly secure manner.

CASE HISTORY NO. 830

Rope-Hook Fatality

Description: A coal car unloader was moving a coal car into position with the use of an electric car spotter, when the hook on the end of the rope slipped from the car and flew back, striking the employee on the right leg. When moving cars in this manner, it is necessary to apply enough brake on the car to keep it from drifting. This means that tension is applied on the rope and then it slackens as the car moves (during this slacken period it is possible for the hook to slip out of position). Prior to this accident a polypropylene rope and smaller hook had been installed; this rope has much more stretch than manila rope.

The injury resulted in a compound fracture to the lower right leg and subsequent death due to embolism.

Cause: 1. Failure to secure equipment.

2. Instructions and training inadequate.

3. Faulty design.

Contributing Causes: The polypropylene rope had been put into use about three weeks before because it was lighter and more durable, and the smaller hook because it had a swivel which would lessen the kinking of the rope. The employee did not have the hook secure and was also pulling from the front of the car. This caused the pull to be from an angle. The employees had not been adequately instructed after the hook and rope had been changed. The hook was too small to hang securely on most cars and the rope had too much stretch.

Preventive Measures: The manila rope was returned to service, a new hook, large enough to fit on the car and lessen the possibility of it slipping when tension is slackened, has been made and put into use.

Reinstruct all unloaders in the proper manner of placing the hook on the car, also to always place the hook on the far end of the car so that if the hook should slip, it would not travel far enough to strike the employee at the control of the car spotter.

CASE HISTORY NO. 831

Equipment Not Properly Prepared for Welding

Description: The bubble cap column, part of the ethyl alcohol recovery system, was shut down approximately 1:00 p.m. Sunday.

Dismantling was begun on Monday, when the old vapor line was removed and a twenty gauge slip blank and a backup flange were bolted to the top of the column to close the system.

On Tuesday, at approximately 12:30 or 1:00 p.m. on instruction from the maintenance foreman because of some doubt about the effectiveness of the gasket used, two mechanics removed the slip blank and gasket from the top of the column and reinstalled the slip blank with a new gasket, using six bolts to tighten the flange.

The riggers then raised the new eight-inch vapor line into position, the one end fitting into the flange on the column and the other end fitting into the flange on the condenser. When the pipe had been placed in position, the department supervisor approved a light-up for the welder. Immediately upon striking an arc to tack weld the pipe, a report was heard. Welding was stopped immediately.

In removing the old vapor line, blanking the column and again removing the blank to replace the gasket, the column had been open to atmosphere possibly two or more hours. It is the opinion of the committee that this provided ample opportunity for oxygen and ethyl alcohol vapors to form a combustible mixture in the head of the column.

In examining the twenty gauge stainless slip blank, the committee found a spot on the blank which indicated it had been very hot and had been struck by a welding electrode; the blank which had been flat on installation was now bulged from the inside out about 1/4 inch.

In discussing the incident with the men involved, it developed that there had been approximately 1/4 inch to 3/8 inch space between the pipe and the flange, thereby giving ample room for the electrode to pass between them and strike the stainless blank, causing it to heat and ignite the mixture in the head of the column. The column apparently was vented through a seal into the building.

Cause: The incident was caused by inadequate preparation of the equipment for the scope of work attempted. No efforts were made to displace the alcohol vapors in the column by any approved cleaning method. It was probably assumed that the twenty gauge metal blank backed by a ring gasket would prevent ignition of any flammable material trapped in the column.

Preventive Measures:

1. Before welding on equipment which has contained flammable liquids or gases, the equipment should be boiled out or thoroughly washed out and vapor tested. Whenever the process and/or equipment permits, it should be filled with water.

2. Where the presence of water in a system is not desirable, proper blanking procedures should be followed and all flammable vapors displaced by an inert gas.

3. The committee strongly recommends that no welding be permitted on equipment known to have contained flammable liquids or gases without preparation of the equipment by an approved cleaning method or the displacement of flammable vapors by an inert gas.

4. On all jobs requiring welding on equipment containing flammable liquid, alternate method of performing the job should be investigated to minimize hazard.

CASE HISTORY NO. 832

Static Spark Fires Vapor During Drum Filling Operation

Description: A helper of the polymerization department was ordered to fill ten 55 gallon steel drums with styrene monomer. This operation is done rather infrequently. A scale was placed near the feed line on which the drums are weighed. When the first drum was placed on the scale and connected to the ground with a spring-loaded clip-type clamp, the department supervisor ordered the electrical maintenance department foreman and an electrician to check with a Megger analyzer if the ground connection was good. They proceeded to scrape the paint on the drum in the place where the clamp was placed. The ground was all right. After this, the filling operation was started. When the sixth drum began to be filled, the helper moved it and a spark occurred between the filling line and the drum, causing an explosion. No fire followed. The supervisor immediately pulled out the feed line; and as he did not close the valve before doing this, the styrene monomer splashed both persons. The supervisor closed the valve. Both persons were taken to the safety showers.

Cause: A spark caused by static electricity ignited the styrene monomer vapors due to a poor ground connection. Negligence on the part of the helper for not scraping the paint off each drum when placing the ground connection. Thoughtless action of the supervisor in pulling out the feed line without first closing the valve, causing the styrene monomer splash.

Preventive Measures:

1. Explain to all personnel the importance of good ground connections while handling flammable materials and the dangers of static electricity.

2. Replace the rigid filling line used to fill the styrene monomer drums by a flexible metallic hose extending to the bottom of the drum.

3. Verify the effectivity of the ground connection of the system before starting to fill drums with the Weston analyzer (low voltage tester).

4. Replace spring-loaded clip-type grounding clamps with screw type grounding "C" clamps.

CASE HISTORY NO. 833

Fatal Burns from Incendiary Compounds

Description: An employee was preparing an incendiary mixture. While adding ingredients, a small amount fell on the framework inside the mixer. Starting the mixer, he raised the lid to brush the material off the framework, and, while doing this, he dropped the lid causing a spark which ignited the ingredients. The flame engulfed him causing first, second and third degree burns. He was immediately hospitalized and died five days later as a result of the burns.

Preventive Measures:

1. All employees of this area have been reinstructed in the approved method of operation.
   a) Operators will not enter the building while the mixer is in operation.
   b) Operators entering the building or handling mix compound will wear protective equipment consisting of aluminum asbestos coat, hood, gloves and safety glasses.

2. The present mixer lid will be replaced with a non-ferrous metal lid.

3. A gate will be installed at the mixing bay entrance with an interlock to the mixer

motor. This will make it impossible for persons to enter the mixing bay while the mixer is in operation.

CASE HISTORY NO. 834

Two Men Burned Operating Steam-Water Mix

Description: Several men were engaged in cleaning the tubes of the air pre-heater at the Powerhouse. They were using three hot water lines which were connected to a manifold of a steam water mixer (aspirator type). Two of the hoses were shut off since they were no longer needed; and at this time, raw steam came out of the third hose splashing the man using it with hot water and steam. He suffered first and second degree burns of the hands and arms. Approximately ten minutes later, in resuming the cleaning operation, another man had his cleaning hose down into one of the tubes when the mixer was turned on. Raw steam came out initially and he was splashed and burned on one wrist.

Cause: The cause of the first of these two incidents was that the steam water mixer is oversized for using only one hose, and that fact plus possible back pressure caused by the shutting off of the other two hoses enabled the steam pressure to close the check valve in the water line, thus permitting only steam to come through the hose. In this case, 200 psi steam and water at approximately 50 psi were being used. In the second incident, the cause was improper procedure in that the hose should not have been in the tube full of water at the time it was turned on.

Preventive Measures:

1. This system of using a large mixer for the operation of multi hoses will no longer be used.
2. The Safety Department will check to see if there is a "safe" steam and water mixer.
3. The Powerhouse will also check to see if there is some point in their operation where they can tap off hot water for use in cleaning tubes eliminating the use of steam water mixers.
4. All other supervision in the plant should check their departments for this type of mixer to see that this same type of thing cannot happen in their areas.

CASE HISTORY NO. 835

Spilled Sulfuric Acid on Foot

Description: The acid plant tank car man was loading a car of 25% oleum in the normal manner using a conductivity probe connected to a bell alarm to determine when the car was full. About 4:00 p.m., the tank car man was standing by waiting for the bell to sound when oleum overflowed out of the dome of the car. The pump was shut off immediately and the car washed down very carefully. The fill pipe and the conductivity probe were removed, the contents sampled and the lid replaced on the dome.

For the loading operation the pressure relief assembly is removed and the conductivity probe is inserted in the air inlet on the dome of the tank car. The pressure relief assembly is fastened to the tank car with a short piece of chain so that it hangs against the side of the dome during the loading operation. When the tank car man attempted to replace the assembly, acid which had collected in a dome shaped section spilled onto his left leg. He immediately got under the safety shower on the loading dock and washed off the acid. While washing, acid and water got inside his rubber bootee through a crack on the top of the bootee burning the top of the foot.

During the investigation it was found that the connection between the conductivity probe and the alarm circuit was poor so that the alarm would not work part of the time. The tank car man had tested the equipment before installing it on the car and had found it satisfactory.

Cause: The primary causes for the injury were:

1. Failure to wash the acid out of the pressure relief assembly hanging on the side of the car.
2. Faulty bootees and insufficient protective apparel.
3. Defective conductivity alarm.

Preventive Measures:

1. Repair conductivity alarm equipment.
2. Emphasize necessity of checking equipment.
3. Replace bootees and emphasize to all employees the importance of having bootees in good condition and properly laced.
4. Instruct all personnel to wear protective clothing when washing down spills of corrosive chemicals.
5. Emphasize importance of thorough washing of any equipment involved in any chemical spill, taking time to double check all parts.

CASE HISTORY NO. 836

Steam-Fitter Cracked Fitting--Line Under Pressure

Description: A steam fitter and an apprentice plumber were attempting to loosen a cast-iron elbow at the plugged end of a four inch pipe. They could not loosen the fitting with a wrench and the steam fitter proceeded to strike the elbow with a hammer to crack it. As he was tapping the fitting, it suddenly fractured and he was struck in the face with fermented steep liquor which sprayed out of the pipe.

Cause: Failure of department personnel to flush out and leave open the pipe lines when they were originally abandoned. The steep liquor which was left in the line, fermented over an eight year period creating excessive pressure in the pipe.

Failure by employee to anticipate the line could be under internal pressure and exercise the necessary adequate precautions.

Preventive Measures: A survey is being made of all existing pipe lines which are not in use to make sure they have been flushed out and cleaned.

Appropriate standard safe operating instructions have been established to relieve pressure from presently existing discarded lines.

Henceforth, whenever personnel work on any discarded lines, proper safeguards will be utilized.

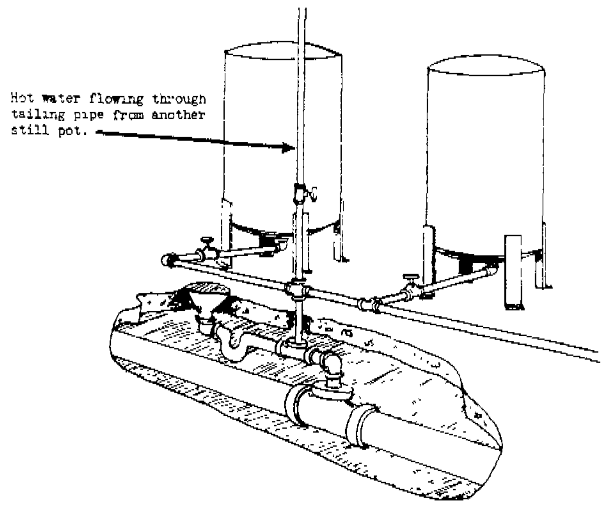
Maintenance Department has made an eye hazard survey to make sure appropriate eye protection is worn during potential exposures.

CASE HISTORY NO. 837

Man Scalded by Flashback from Floor Drain

Description: A series of still pot dumping lines are connected to a floor drain line. The valve from the last still pot, however, is directly over a floor drain. Hot water tailings were flowing into the connection to the sewer line and probably heated the water in the trap of the floor drain. As the operator opened the valve, standing over the floor drain, the still bottoms rushed into the sewer, causing some of the hot material to gush out of the floor drain, scalding him about the thighs.

Preventive Measures: The dumping line and valve can be easily rerouted from the opposite side of the still so the operator is protected. The department is surveying all other such connections to sewer lines and taking corrective action where necessary.



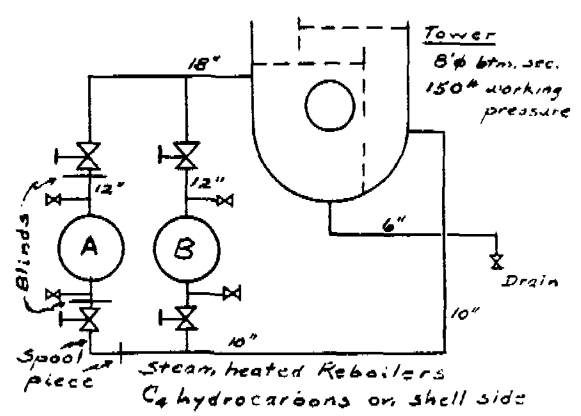
CASE HISTORY NO. 838

Flash Explosion in Bottom of Eight-Foot Diameter Fractionator

Description: At 11:00 a.m. an explosion occurred in the bottom of an eight-foot diameter fractionation tower which handles hydrocarbons in the normal butane boiling range. The incident occurred while the tower was undergoing a turnaround started some two weeks previously. One man was in the tower at the time. He survived the explosion, but died in the hospital 10 days after the incident.

The tower was prepared for a turnaround by steaming out and blinding off all inlet and outlet lines. The sudden occurrence of a gas in the bottom section of the tower after two weeks downtime was completely unanticipated.

The tower is equipped with two reboilers which are heated by 15-pound steam with the hydrocarbons on the shell side as shown on the sketch. Either reboiler can be isolated by a 10-inch inlet valve and a 12-inch outlet valve. There had been a fouling problem with these reboilers, and the valves were installed originally so that



either tube bundle can be removed while the tower is in operation.

Some time before the shutdown and while the tower was in operation, reboiler bundle "A" was prepared for pulling out of the shell by closing off on the shell side of the valves. Hydrocarbons in the shell were vented off and the shell side filled with water and drained. After unheading, the bundle was pulled out and prepared for cleaning. Later the tower was shut down and prepared for entry as previously described. During the turnaround "B" reboiler bundle was also pulled out for cleaning. Both bundles, after cleaning, were reinstalled in the shells and pressure tested with water by inserting additional blinds on the shell side of the valves in the "B" reboiler. After testing, the blinds were pulled.

On the morning of the incident and before the start of the shift, the tower was checked for explosive gases, and none were found. Later, the water was drained from "A" reboiler by removing the spool piece marked on the sketch below "A" reboiler. Although there was a small drain valve available above the block valve, it is the normal practice to examine this spool piece in case there are rubbery deposits.

Cause:

1. The explosion occurred shortly after water had been drained from the "A" reboiler. The bottom manhead was open at the time of the explosion. The severity of the explosion was such that a number of trays in the bottom section of the tower were lifted. Investigation showed that the water from the reboiler contained gas so the foreman went up to the manway to check the condition of the tower. As he looked into the manway, the explosion occurred. The foreman was burned about the face, but not critically. The man in the tower managed to reach the manway and was pulled out. The source of ignition was created when the man in the tower broke the safety electric light. It was of the type with an outer protective cover. This was an approved fixture, vapor-tight, with a heat-treated vapor globe and metal guard.

2. Investigation was started immediately to determine the source of the gas. It was reasonably certain that gases were trapped in the "A" reboiler and piping as a pocket or absorbed in rubbery deposits in the piping or minor deposits in the shell of the reboiler.

3. Close scrutiny of the events just before the explosion led us to the following conclusions: When "A" bundle was pulled while the tower was operated, and the block valves closed, liquid hydrocarbons remained trapped in the bonnets of the gate valves. As standard shutdown procedure, the tower and piping were completely filled with water. Thus, the piping above "A" and "B" reboilers and above the outlet block valves were completely free of gas. When the operator drained "A" reboiler, he opened the block valve above the reboiler as a vent so that the water drainage was facilitated. When this valve was opened, the residual hydrocarbons in the bonnet were vaporized and entered the tower through the 18-inch line between reboiler outlet valve and the tower.

Preventive Measures: Incidents of this type can be minimized by taking the following precautions:

1. Blind next to the vessel without including block valves within the blinds.

2. Where gate valves are included within the blinds, they must be opened during the flushing and purge period and remain open to avoid liquid hydrocarbons trapped in the bonnet.

3. Do not include reboilers or vessels which contain rubbery deposits within the blinding schedule. The rubbery deposits contain hydrocarbons (similar to activated carbon) which can be displaced by water and released over a period of time.

4. There should be a better constructed extension light with an unbreakable globe.

CASE HISTORY NO. 839

Sodium Chlorite-Oxalic Acid Mixture Explodes

Description: A laboratory assistant was preparing to bleach a 20-yard length of synthetic fabric. He had entered the fabric into the appropriate machine and was preparing the bleach liquor to be employed. He placed a weighed quantity of sodium chlorite in an empty stainless steel beaker, added a weighed quantity of oxalic acid and was just beginning to add water when he noticed the mixture beginning to fizz. He stepped back and immediately afterwards the contents of the beaker exploded violently. The solid material resulting from the explosion was flung up to the ceiling, and sprayed an area extending up to 10 feet around the seat of the explosion. A large amount of chlorine dioxide gas was evolved and all laboratory windows were immediately opened and the room evacuated. Fortunately, a stiff breeze was blowing and this soon cleared the atmosphere in the laboratory. The area of the explosion was then completely washed down with an adequate quantity of water.

Cause: Sodium chlorite is a very strong oxidizing agent and must be handled with care. It can react almost spontaneously with readily oxidizable material, e.g., cellulose, oxalic acid. In dilute solution it is not explosive but is quite corrosive. Acidified solutions of sodium chlorite generate chlorine dioxide gas which is similar to chlorine gas in its physiological action.

In ignorance of the above facts, the employee mixed solid sodium chlorite with solid oxalic acid and the explosion resulted.

Preventive Measures:

1. All members of the laboratory staff have been advised of the cause of this occurrence.

2. The sodium chlorite container which was old and tarnished has been relabeled and a warning appended thereto requesting persons to read the appropriate literature before using the chemical.

CASE HISTORY NO. 840

Yellow Phosphorus Ignites Clothing

Description: The injured employee was batch loading solid yellow phosphorus from a drum into a 1000 gallon reactor. During the handling of the 10 pound phosphorus wedges, a chip (approximately bean size) of phosphorus struck the lower left leg of his trousers and ignited. He received a severe burn to the lower left leg.

Cause:

1. Small chips of phosphorus are known to be lying on the larger wedges and/or they may break off the wedge during handling. These small chips will ignite when they become dry and exposed to air.

2. After a period of operating without incident, supervision and employees became lax in the use of the specified protective equipment.

Preventive Measures:

1. Supervision will institute a regular "safety audit of hazardous operations."

2. The necessity for additional personal protective equipment during especially hazardous jobs, even of short duration, will be emphasized.

3. The length of the raincoats will be increased, or the use of two-piece rubber suits will be instituted for additional protection.

4. The area for changing clothes will be relocated to eliminate congestion.

CASE HISTORY NO. 841

Blowing Agent--Flash Fire

Description: A fork lift truck operating in a storage warehouse struck one of six fiber drums containing a blowing agent. The operator reported that there was a "shot of flame from the material when the drum broke." Thirteen sprinkler heads operated, extinguishing the ensuing fire. Building damage was minor, due to the automatic sprinkler system and good building construction. The relatively small dollar loss resulted for the most part from water damage to the stock, consisting of a wide variety of raw materials used in the rubber and plastic products manufacturing plant.

Cause: The source of ignition was not immediately determined, but no doubt was caused by friction when the fiber drum was penetrated or broken by the truck. The blowing agent involved was a mixture of 40% dinitrosopentamethylene tetramine and 60% inert (fine silica). The active ingredient, which decomposes slowly to release nitrogen under controlled heating, is quite flammable in the dry state, and can be ignited by friction or direct flame. It burns very rapidly once ignited, and probably would not be extinguished by any ordinary means.

Preventive Measures: Store in sprinklered area cut off from other storage. Store in rows not over two pallets high and three pallets long, away from steam pipes or other heat sources. Leave four foot aisles between pallet rows, with ten foot minimum every fourth aisle. A high degree of cleanliness should be observed in warehouse and operating areas. Never open drums in the storage area, and limit amount on hand in operating area to one day's supply.

CASE HISTORY NO. 842

Power to Pump Turned Off But Not Locked Out

Description: There was a sub-standard batch of viscose in #14 churn. An attempt was made to pump this batch into a dempster car through the normal waste line but it was too heavy and the transfer pump was jammed. The next step was to attempt to get the viscose back into the churn by use of vacuum so that it could be diluted. The injured employee, a millwright, was attempting to back up the pump in order to relieve the jam by using a 24-inch pipe wrench on the pump shaft. Another engineering employee passing through the area, was requested to turn on the vacuum. This employee misunderstood the request and instead started the pump. The handle of the pipe wrench which had been applied to the pump shaft, flew around, striking him in the jaw and resulted in laceration of his jaw and loss of three teeth.

Cause: The employee failed to tag out the pump before attempting to rotate its shaft with the wrench. Operating personnel had been assigned to assist, but were carrying out other duties. The injured employee, instead of waiting for his return, requested assistance from a passing employee.

It is believed that the primary causes of this accident were:

1. Failure to secure the equipment by locking out the starting switch.

2. Instructions were inadequate.

Preventive Measures: A group safety meeting was held and all employees were instructed to follow safety procedures regardless of the nature of the job or length of time that would be required for its performance.

It was especially stressed as being important that lock-out and tag-out procedures be followed without fail. Such procedures are designed and provided to prevent injuries and cannot be omitted at the whim of the employee. They must be used each and every time, rather than being used only when it is felt that the job will be long enough to merit it.

CASE HISTORY NO. 843

Loaded Gun--Oxygen in Nitr gen-Purge Supply

Description: A process difficulty was traced to a nitrogen purge supply received from a liquid nitrogen storage tank. Subsequent analysis disclosed 18% oxygen in the nitrogen. The nitrogen storage tank was thereupon vented, purged with nitrogen and refilled with additional nitrogen.

A trailer of liquid nitrogen had been unloaded earlier in the day. Prior to unloading the trailer, a plant employee had used a portable oxygen analyzer to test the nitrogen and reported the test indicated no oxygen.

Cause: The supplier was contacted after the incident, and, upon investigation, determined that a quantity of liquid oxygen had been loaded into the liquid nitrogen trailer.

The oxygen analyzer was found to be inoperative when checked during the investigation. A review of the technique used by the employee handling the unloading also disclosed he was not familiar with the procedure for checking out the analyzer.

Preventive Measures: The supplier was asked to study his method of loading nitrogen and report the action that would be taken to prevent a repetition of the incident. It was suggested that the nitrogen trucks and loading facilities be equipped with special fittings different from oxygen.

The supplier will be requested to supply a certificate of analysis for each truck of nitrogen delivered to the plant.

Prior to unloading liquid nitrogen trucks the contents will be tested for oxygen content by two independent methods, one to be used by the employee responsible for unloading, the other to be performed by a member of shift supervision.

Regular retraining and checking of procedures for using gas-testing instruments will be set up for wage roll and supervisory personnel using these devices.

The feasibility of continuously monitoring the oxygen content of the liquid nitrogen storage will be investigated.

Editor's Note: In sampling and analyzing for oxygen under such conditions, one should remember that liquid nitrogen boils at minus 195.82°C and that liquid oxygen boils at minus 182.97°C. For this reason the gas phase above a liquid mixture of oxygen-nitrogen will contain negligible oxygen until essentially all of the nitrogen has boiled away. Gas sampling can, therefore, be quite misleading. One quick test consists of allowing a portion of the liquid mixture to boil and observe the color of the liquid. If oxygen is present, a bright blue color will develop as the ratio of oxygen to nitrogen increases.

We are sure that this relationship has not been overlooked, but consider the potential danger involved to be great enough to warrant emphasis on this point.

CASE HISTORY NO. 844

Nitroglycerin Neutralization--Operator Confused—Tries to Cover Up Mistake--Then Panics

Description: The foreman was notified by the nitroglycerin neutralizer operator that the charge was not settling out properly after neutralization. They proceeded to the tank (Tank No. 3) which contained a normal volume, but there was only about 5 inches of soda water above the nitroglycerin layer. After bringing the charge up with air again and "pulping", the same amount of soda water was above the nitroglycerin layer. On questioning the operator, the foreman learned that he had prepared Tank No. 4 to receive a charge of UNG, and the nitrator man called and said that he would ship the charge in 5 minutes. The operator turned the air agitation on, but turned the agitation on to Tank No. 3 instead of Tank No. 4. Shortly thereafter, he realized the air was on Tank No. 3

and the hose set to Tank No. 4, so he moved the hose to Tank No. 3 which had the agitation on. He proceeded about his work and then realized his error and threw the hose back to Tank No. 4 while the nitroglycerin was coming in. He neutralized the UNG in Tank No. 4 after bucketing about 4 inches of soda water from No. 3 Tank. It was later discovered that the thermometer was broken during these proceedings.

Cause: This was a case of an operator becoming confused, then panicking and trying to cover a mistake. The operator had just recently finished his complete nitroglycerin training.

Preventive Measures:

1. The operator was removed from the job of nitroglycerin operator and placed on his permanent job of magazine helper, with the understanding he would not work with nitroglycerin again. This incident emphasizes the importance of careful selection of personnel for critical jobs and the need for corrective measures when in doubt as to capabilities.
2. The building, tanks and hoses were washed several times with hot water in order to decontaminate from any spilled nitroglycerin or foreign materials.

CASE HISTORY NO. 845

Ammonium Perchlorate Casting Ignited During Hand-Cutting Operation

Description: Two operators were cutting laboratory test specimens from a 92-pound cast ammonium perchlorate propellant grain. Beryllium alloy knives were used to obtain the specimens, utilizing only the pressure afforded by one hand on the knife. In the course of cutting, both operators simultaneously observed sparks at the point of cut and promptly evacuated the cell. There were no injuries. However, the grain burned so rapidly that flame singed the hair on the back of one operator's head as he was departing the cell. The automatic deluge system functioned as designed. Damage was negligible. About forty similar specimens had been previously taken from the same grains, with hand knives, without incident.

Cause: Ignition is attributed to the friction inherent in the cutting action.

Preventive Measures: Design studies have been initiated to determine the feasibility of providing remotely controlled machine tooling that will cut specimens of any desired shape from perchlorate propellant grains.

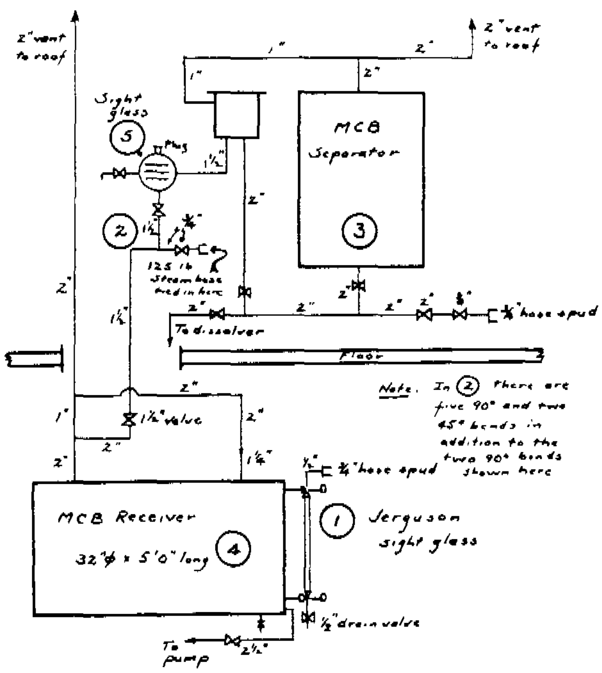
CASE HISTORY NO. 846

Pressurization of Uncoded Vessel Causes Rupture

Description: (See Sketch) An area maintenance mechanic was attempting to clear a plugged product feed pipe line (2) connected from a separator (3) to a vented horizontal receiver (4) located on the floor below. He had cleaned out the sight glass (1) and was attempting to steam out the product pipe line which was still plugged. He connected a high pressure steam hose from a 125 psi steam header to a coupling on the product line on the second floor below the overflow sight glass (5). He closed the valve underneath the sight glass and opened the valves on the product line and the steam header applying steam to the product line. When last seen, the mechanic was standing on the receiver feeling the temperature of the pipe. A short time later the receiver suddenly ruptured at the east end and the mechanic was injured, fatally.

Cause: Failure to recognize, by those directly and indirectly involved, the potential hazards existent in this cleanout practice.

The horizontal receiver was an uncoded vessel. (Calculations made after the accident indicated that with all available venting unrestricted a 6 psi pressure could develop from a sustained flow of 125 psi steam through the product line. The receiver, when new, would have failed at about 13 psi. Corrosion had weakened the vessel to some degree and available venting was significantly reduced by product buildup. When steam broke through the blocked product line the venting



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system did not release the steam rapidly enough to prevent a pressure buildup to the fail point of the receiver – under 13 psi.)

Preventive Measures: Engineering changes have been made in the process and equipment which completely eliminates the need for a horizontal receiver, and the product is piped directly from the separator into the process.

A comprehensive survey is being made of all plant operations involving pressure to assure pressure requirements use (high pressure steam especially) are kept to within safe use limits.

Employees have been reinstructed to note on the operating log sheets any abnormal occurrences including plugged lines and steaming operations.

This accident has been reviewed (at the scene) with all plant supervisory personnel.

CASE HISTORY NO. 847

Carpenter Opens Acid Line-- Four People Injured

Description: The accident took place on the operating floor of the A.C.D. mixing unit, within the cubicle containing the acid-measuring tank to the mixer. The tank and auxiliary equipment had been out of service for a year and removal was underway. At the time of the accident, only a 2-inch lead acid delivery line remained to be dismantled, and had been assigned to two pipefitters as part of their day's schedule.

The lead line, which had delivered 93% sulphuric acid from an outside storage tank to the measuring tank, ran horizontally at floor level across the back of the operating floor, up the wall and then ended in a 180° bend at the discharge to the tank. The maximum height of the bend was 6 feet above the floor, with the open end of the pipe about 5 feet above the floor.

A carpenter and helper were repairing a section of the wooden floor across which the pipe ran, and nearby two pipefitters were installing an air line to the mixer. All were wearing hard hats, and safety glasses with side shields. The two pipefitters assigned to the lead pipe removal were still working in another area.

The carpenter, having bumped his head against the bend-over of the lead line, considered the line a hindrance, and asked the pipefitters about it. Upon being told the pipe was to be removed, he decided to cut the pipe himself.

At a spot where the pipe crossed the floor horizontally, the carpenter, facing his fellow workers, cut 3/4 of the way through the pipe with one blow of an axe. On removing the axe, acid sprayed forward a distance of approximately 8 feet, hitting one pipefitter in the back of the neck and shoulders, and the other in the face as they worked together threading pipe. The carpenter hurriedly put his foot over the spray, but deflected spray onto the elbow of his helper working on the other side of the cubicle. The pipefitters and helper immediately went to the nearest shower. The carpenter dropped down through a wall opening and followed, but had to find room at a further shower. Following 30 minutes showering, all four men received treatment at the Plant Hospital, and returned to work.

Cause: The line, leaving the outside 93% sulphuric storage tank, travels to a pump and valve, then underground to the A.C.D. building, and up along the ceiling to the mixing floor.

When the use of the equipment was stopped a year ago, the valve at the pump end of the line was closed, and a blind flange attached to the inlet side of the valve. The line itself was never drained, hence acid remained in the line from the valve to the highest point in the 180° bend at the mixing unit. The spray was caused by the 5-6 foot head of acid in the open-ended line above the cut.

The carpenter, who had no specific training for work on acid lines, had no authority to cut the line and further used an unorthodox tool and method. This work had been assigned to two qualified pipefitters, experienced with acid lines, who would normally have checked the line for residual acid before proceeding with dismantling.

However, at the time of the accident, no one was aware that the line had been left full of acid, and the work area in general was considered safe.

Preventive Measures:

1. The equipment has now been removed so no equipment changes are required.
2. For a lengthy equipment shutdown, any process liquid line should be immediately drained and blown clear and blanked off at both ends.
3. The accident will be discussed with all plant personnel stressing:
   (a) The value of safety equipment,
   (b) The necessity for always assuming an acid line is full,
   (c) The potential hazard in performing unfamiliar work outside the work assignment,
   (d) The use of proper tools and proper methods at all times,
   (e) The need to be constantly on the watch for "booby traps."
4. All members of supervision should always be on the alert to avoid the creation of "booby traps," one of which (the failure to drain a line taken out of service) laid the foundation for this incident.
5. The importance of issuing proper instructions to craft employees.

6. The importance of wearing personal protective equipment as a means of avoiding personal injuries is also evidenced in this occurrence, and this fact should be emphasized to all employees.

CASE HISTORY NO. 848

Exposure to Temperature Extremes

Description: An employee was attempting to clear a transfer line containing solidified calcium chloride by intermittently steaming and washing. Being unable to clear the line by using the fixed connections, he decided to insert a hose with running warm water into the open head of the spare pump discharge line. He opened a four-inch valve and pushed the hose into the vertical section of this line. There was a sudden release of hot water and calcium chloride due to a head pressure on the line. Hot liquids gushed out the spare pump open head onto the employee, burning his right leg and arm.

Cause: 1. Molten 40% calcium chloride leaking through a closed 6-in. gate valve plugging the transfer line.

2. Using an unsafe procedure for unplugging the line by standing in path of open pump head and inserting a hose with running warm water through open pump head into the plugged 6-in. vertical pipe.

Preventive Measures: 1. Plant personnel will be re-instructed to keep to recommended procedures for thawing and washing lines. These procedures are as follows:

a. All lines on shut down will be flushed and/or drained to prevent freeze up.
b. Steam directly connected to lines will be used where necessary to clear obstructions from lines.
c. Water washing to clear solidified obstructions will be handled by cutting a hole or holes in the line so a copper tubing with running water can be inserted to erode or thaw the solidified calcium chloride.

2. The spare pump head and its accessories will be removed.

3. The steam-out connection which is also a vent opening will be enlarged (1/2 x 1 in.).

4. A preventive maintenance program will be established to eliminate leaky valves.

CASE HISTORY NO. 849

Five Employees Burned by Molten Metal

Description: Five employees were functioning as a work crew to cast 5-1/8 in. diameter aluminum logs by direct chill casting process. In the process, molten aluminum is released from a taphole of the casting furnace and flows into a trough extending over a casting distributor pan. A ceramic down spout located in the bottom of the trough permits the further flow of molten aluminum into the casting distributor pan, which then channels the metal to 12 open molds fixed in circular arrangement within a water-tight table beneath the casting pan. During the casting process, cold water circulates within the water-tight table to chill the sides of the casting molds and molten aluminum entering each of the molds immediately "freezes" and begins to descend on a hydraulic elevator into a pit. At the finish of the cast, 12 aluminum logs of 5-1/8 in. diameter and 13 ft. of length are thereby produced.

During the process, the flow of molten aluminum is controlled at two points. The first by a plug at the furnace taphole and the second at the ceramic down spout where a screw-type metering control rod is fixed above the spout. Each of these controls is manually operated to independently vary the rate of flow of metal into the trough and the casting distributor pan.

From the start of shift at 11:00 p.m., the employees had already completed one casting cycle for production of aluminum logs. In this first operation, they successfully cast 10 logs and then prepared to set up for a second casting cycle. The five employees were all positioned around the casting equipment and had tapped the furnace for flow of metal into trough, casting pan and molds.

Cause: As the metal level in the trough increased, the flow from the down spout into the casting distributing pan functioned sluggishly. To permit greater metal flow into the pan, the foreman further adjusted the metering control rod to a more open position. However, the adjustment still did not permit adequate flow of metal into the pan and there appeared to be some obstruction within the throat of the ceramic down spout. The foreman then withdrew the metering control rod and inserted a steel rod into the down spout to release the obstruction. At once, molten metal gushed forth from down spout overflowing the casting pan. Before the foreman could reinstruct the metering control rod, the overflow molten metal came in contact with water seepage which had collected in a recess beneath the casting pan and the surface of water-tight table. Minor explosion then followed which blew casting pan and molten metal from the water-tight table, causing molten metal to splatter employees.

All five men received burns to the face and body. The burns to one man were diagnosed as critical, two others as serious and the remaining two as satisfactory.

Preventive Measures: 1. The surface of water-tight table to be kept perfectly dry at all times. Water seepage from molds onto table surface has been eliminated by water-tight weld of flange to mold and insertion of O-ring gaskets around mold flange.

2. Entire surface of water-tight table and casting pit has been painted with Rust-Oleum to reduce condensation.

3. Size of casting pan to be enlarged to accommodate more metal. Metering control rod and down spout equipment to be thoroughly checked for proper opening, prior to start of each casting cycle.

CASE HISTORY NO. 850

Chemical Engineer Burned-- Jacketed Kettle Collapsed

Description: The chemical engineer was supervising the production of a batch of special synthetic size. One production batch had been completed without incident. During the start up of the second batch one of the raw material product pipe lines plugged as a viscolizer pump was started up. A mechanic attempted to thaw the line by heating it and the viscolizer pump with a propane torch.

While the mechanic was attempting to unplug the product line, the engineer walked over to the production kettle and lifted the cover to inspect the contents. Deciding that the melted product in the kettle might be cooling off, he partially opened the steam valve on the jacket which had been shut just 15 minutes before. As he started to walk away, the inner wall of the kettle suddenly collapsed and hot molten material gushed out of the loose manhold cover spraying the employee and the mechanic.

Cause: Failure of the inner wall of the kettle was possibly caused by excessive steam pressure, metal fatigue, or was due to an explosion of vapors which might have entered the jacket through the steam outlet as the kettle was cooling. (The production kettle is a 100 gallon jacketed stainless steel vessel. The working pressure on the jacket is listed at 47 psi and there was a 75 psi relief valve on the jacket. A 3/4-in. 125 psi steam line was directly connected to the jacket.) Procedure for applying steam to the jacket was to partially open the 125 psi steam valve and close it when the relief valve popped. Continued opening and closing of the steam valve might have fatigued the jacket wall, since the steam pressure applied was higher than recommended for the jacket. (The relief valve was last inspected in 1959 and on the test after the accident the relief valve opened at 75 psi.) Further investigation to determine the specific cause for the vessel inner wall collapse is presently being carried on.

Preventive Measures: On the replacement installation a reducing valve has been installed on the steam line to the jacket to assure steam pressure on the jacket is in accordance with the listed working pressure. Also, another outlet on the jacket has been fitted with a gauge to make sure jacket pressure can be accurately checked.

The condensate from the jacket has been trapped and a check valve has been installed in the line before it discharges to the drain. This will assure no back up of vapors from the drain into the jacket.

Additional steam tracing and Infra-red heat lamps have been added to the product lines and pump to eliminate the need for thawing out plugged lines with a propane burner.

All vessels will be equipped with direct reading temperature indicating instruments in accordance with Safety Standard for Methods and Equipment S24 and Appendix S-24 A "Reaction Temperature Controls," and the vessels will be water pressure tested at 1-1/2 times the working pressure before used.

CASE HISTORY NO. 851

Pressure Shock Resulted When Valve Was Closed

Description: Employee was changing the flow direction of phosphoric acid from a centrifuge to several locations. As he was closing a valve in a pipe line leading to a tank car, a short rubber hose connection leading from the centrifuge blew off its nozzle and sprayed the employee with acid.

Cause: Failure of employee to open one discharge pipe line before closing off another caused excess pressure on a weak connecting section of pipe.

Failure of employee to wear eye protection while opening and closing acid valves.

Preventive Measures: A rupture disc and return line to the centrifuge sump has been placed in the discharge pipe line between the centrifuge and the acid loading lines, to protect lines from excessive pressure and personnel from any resulting acid spray.

Operation work procedures have been made up and posted.

Henceforth, employees will wear eye protection when operating or working on acid valves.

CASE HISTORY NO. 852

Fire and Explosion--
Organic Peroxide Compounds

Description: A shipment of organic peroxides aboard a tractor-semitrailer combination caught fire and exploded at approximately 1:20 p.m. on April 3, 1962, during unloading operations. The shipment consisted of 37,900 pounds (not including container weights) - 17,150 pounds benzoyl peroxide; 18,000 pounds lauroyl peroxide; 2,400 pounds cadox MSD (methyl ethyl ketone peroxide); 350 pounds cadox TBH (tertiary-butyl peroxide). Unloading operations commenced at approximately 12:50 p.m., and 50 pound cartons of benzoyl peroxide were being unloaded and placed upon pallets on the platform. A fork lift truck was employed to remove the loaded pallets to the storage building. After 6 or 7 pallet loads had been removed, the driver and 2 warehouse employees saw gray-white smoke billowing over the top of the lading, apparently from fire in the front of the trailer. They shouted to other employees that the truck was on fire. One employee notified the fire department, including the information that the truck contained explosive chemicals. This call was recorded at 1:22 p.m. Meantime, the driver sent an alarm from a fire alarm box located on a pole near the truck and this call was recorded at 1:25 p.m. The driver and a warehouse employee indicated that as soon as they saw the heavy smoke coming from inside the cargo compartment, they went immediately to the front of the semi-trailer and observed no evidence of fire there at that time. The driver started to detach the tractor from the semitrailer, but refrained when he heard a series of muffled explosions in the cargo compartment. About this time, several persons noted flames and smoke coming from the underside of the van, near the front, and the building was evacuated as quickly as possible. The fire trucks arrived within a few minutes and a warehouse official notified them that the truck and building contained explosive chemicals. Firemen laid 2 hoses to the rear of the warehouse and took up positions to the rear of the loading platform, the 2 groups standing approximately 30 ft. apart at angles of 20° to 30° on each side of the open doors of the semitrailer. It was intended that the two streams of water be crossed at the back of the trailer, causing a heavy spray effect throughout the cargo compartment. The water was turned on and after the stream of water had been played upon the fire for approximately 1/2 minute, there was a muffled explosion - then a tremendous blast. The explosion demolished the truck, caused extensive damage to the buildings and surrounding property, and is reported to have broken windows more than 1/2 mile from the scene. Fire immediately engulfed the entire building area, including the fire-fighting equipment. All buildings and vehicles were completely destroyed. Casualties included 4 firemen killed, 2 firemen injured, and injuries to 3 warehouse employees. The warehouse buildings consisted of 2 main structures, several small sheds and service buildings. The north building was a 2-story frame structure with asphalt siding, 175 ft. long and 42 ft. wide and a small brick boiler room was located near the north end, adjoining the east side. The south building was a 1-story brick and concrete structure 75 ft. long and 30 ft. wide, with 2 small sheds attached to the south end. A space approximately 35 ft. wide separated these two main buildings, providing an area into which vehicles could be backed for loading and unloading at a concrete platform situated at the rear of the buildings. The truck was parked at this platform when the fire and explosion occurred.

Comment: A national fire authority had conducted tests of various peroxides, including those involved in this incident, and stated that each of the compounds is hazardous by reason of high active oxygen content which directly supports combustion and explosion processes, even though air is excluded. These tests showed that of those involved here, lauroyl peroxide was the most difficult to ignite, and burned slowly and incompletely. Methyl ethyl ketone peroxide and tertiary butyl hydroperoxide were found to ignite readily under various conditions and burn vigorously. This authority found, however, that benzoyl peroxide (solid) was extremely sensitive. It ignited under 20% of the flame exposure required for black powder, and under moderate impact, pressure or heat, and decomposed very rapidly with explosive violence, depending upon the size of the sample and extent of confinement. Several serious explosions or fires resulting from the handling of benzoyl peroxide were cited: In one instance, loose granules being swept up with a broom ignited causing a costly fire; in another case a 300-pound shipment of this compound was exploded as the truck on which it was being carried was sideswiped by another vehicle; in other instances, fire or explosion occurred when the product was subjected during ordinary handling to small sparks or overheating.

Cause: Investigation of this accident was difficult because of total destruction of the vehicle and its contents. Every effort was made to account for the handling of the shipment from the loading of the vehicle at its origin, to its arrival at the warehouse where it was to be unloaded, and to obtain complete description of events which preceded the fire and explosion while the vehicle was at the warehouse. The trailer was sealed at the shipper's plant, and traveled the 550-mile distance to destination without reported incident. The seal was not broken until the vehicle arrived at destination and just before unloading began. The only reported situation in which the cargo might have been subjected to stress occurred as the driver crossed a raised sidewalk, which caused the combination to yaw and lurch. However, this occurred more than an hour before the unloading operation began. The possibility exists that the cargo may have been subject to an impact shock as the truck was backed into the dock, or that some of the cartons fell from an upper to a lower level during the unloading process. It was not possible to make any determination of the containers used in this shipment because of the total destruction; however, with the cooperation of the consignee, stocks of the same products in their usual shipping containers at another warehouse were examined and found to be packed in accordance with ICC specifications and carried the required labels. Records indicated that the vehicle had received regular inspection and maintenance and was apparently in good mechanical condition. Consultations were also held with well-informed chemists and other specialists of major fire prevention organizations. Despite these efforts, it has not been possible to determine the cause of ignition of the cargo.

Preventive Measures: This accident demonstrates the extent to which materials commonly shipped in commerce are charged with unusually hazardous properties. It serves to emphasize the vital importance of taking all precautions to assure that such articles are loaded and handled strictly in accordance with established regulations and good practice.

CASE HISTORY NO. 853

Thiocyanate Solution and Nitric Acid--Violent Reaction

Description: At approximately 6:00 a.m. on July 6, 1962, the trim line in the solutions area ruptured. The line is 3-in., 304 SS, Schedule 40. The rupture occurred at the ell on the riser before the horizontal run to the blend tank inlets. The analysis of the blend in tank F-4 showed it was ready to pump except for a slight adjustment in pH. The acid pump was started, the valve opened at the trim line and acid pumped into tank F-4. At this time, the circulation-transfer pump was running. The valve on circulation line was then closed off as line to tank F-6 was opened. The operator then went to the top of the blend tanks to set valves for the blend being made in tank F-5. He opened the trim line valve into tank F-5. After doing this, he opened the thiocyanate block valve at its connection into the trim line. He then went to the control house and shortly after arrival there, the line ruptured. One missile (9in. x 3-1/2 in.) was found at a point approximately 50 ft. northeast of the break. The block valve at the circulating-transfer pump outlet was also damaged. One portion of the split gate was bent and the bonnet gasket was blown out. When the pipe ruptured, the vertical portion was thrown into the tank (F-4) causing a caving in of an area approximately 14 ft. in circumference and a tear through the tank approximately 4 in. in length and 1 in. wide. The weld on the trim line inlet nozzle was cracked on the north side. The weld on one leg of the platform was broken loose. The pipe support on the tank foundation was bent and both the air and steam pipes attached were bent.

Cause: The trim line was full of acid when the thiocyanate was blown in. The oxidation reaction of thiocyanate and nitric acid was checked out in the laboratory, and a violent reaction occurred.

Preventive Measures:

1. Immediate repiping of the thiocyanate line, removing it from the trim line and putting it into the manheads of the tanks.
2. The following revised operating instructions were issued:
   a) At no time will trim be added unless the circulating pump is in operation.
   b) Thiocyanate addition: When a blend is finished and the laboratory man has taken a sample, the thiocyanate should be added through the line at the manhead.
      1) Turn on air agitation in blend tank.
      2) Add thiocyanate.
      3) Keep agitating until blend is approved for pumping or trim.
      4) If blend is satisfactory, take an additional sample for the laboratory to check thiocyanate concentration. Then pump to storage.

CASE HISTORY NO. 854

Inhaled Hydrogen Sulfide Fumes and Collapsed

Description: While attempting to charge an additional two carboys of inhibited 18° Be muriatic acid to the 401 metallizer, the metallizer operator noticed a back flow into the charging tub. Upon investigating the tub closer to be sure it was rising in level, he received hydrogen sulfide fumes directly in his face. He immediately became light headed and dizzy. Before evacuating the area to seek help, he closed the valve to the charging tub to prevent filling the area with more hydrogen sulfide fumes. For this action, he is commended.

After the valve was closed, he headed for the stairway to the second floor control room where help could be obtained. Half way up the stairs he collapsed and fell. Fortunately, his foot caught between the stair treads and prevented his falling backwards down the remaining stairs. No injury was sustained by this fall.

Regaining consciousness, he pulled himself to his feet and proceeded up the stairs. At this point, the premium operator noticed he was in trouble and assisted him back down the stairs to the dispensary.

After receiving treatment at the dispensary, he returned to his job and completed his shift without further trouble or ill effects.

Cause: It is normal procedure in this department to periodically clean out a residue in the metallizer kettles with a kerosene - inhibited muriatic acid-water solution. The water is added to the kettle through a hose from a utility station whereas the kerosene and muriatic are premixed by manual addition in a stainless tub and fed into the system through a hose at the suction of the metallizer circulation pump. The tub is located on a pallet and raised with a transtacker to an elevation above the suction of the pump to provide a positive suction head. If additional acid is required, the above procedure using the tub and transtacker is again used.

The cause of the accident was due to the level of the wash solution in the kettle being greater than the height of solution in the tub. When the valve between the tub and suction line was opened, a flow of hydrogen sulfide saturated wash solution started into the tub and subsequently evolved the fumes that caused the accident.

The vent on top of the metallizer was open as reported by the injured and no sign of pressure buildup was apparent at the time of the fumigation.

Preventive Measures: Specific:

1. Provide a check valve on discharge of stainless tub to prevent backflow from metallizer.

2. Institute operating procedure whereby the 6 in. valve in the pump suction line under the kettle is closed before connecting the hose from the charging tub to the suction line.

3. Be sure pressure gauge on kettle registers zero pressure and vent line valve is open before opening the valve on the discharge of the stainless tub.

4. Provide exhaust blower or steam jet to vent vessel. Discharge of blower or jet to extend above roof level.

5. Provide Scott "Ska-Pak" for personnel doing washing operation. This device provides a five-minute air supply and is carried like a canteen without interfering with personnel working mobility.

6. Make effort to charge acid on day shift if possible.

General: Review other operations in the plant to determine if there is a possibility of sudden fumigation from sampling, tank gauging, equipment cleaning and opening. Departments where such a situation exists should be provided with Scott "Ska-Pak" equipment. This equipment is light, does not interfere with the carrier's mobility, and provides a five-minute air supply for escape or quick recovery purposes only.

CASE HISTORY NO. 855

Near Serious Injury--Working Inside Tank--No Tank Entry Permit

Description: Three maintenance men were in the process of installing a new cooling coil in the #1 Aroclor Chlorinator. The installation of this one and one-half inch diameter coil involved the lowering of the coil from the open upper head into the chlorinator and then the bending of the vertical discharge riser through a side nozzle on the chlorinator. The injured entered the chlorinator to apply heat with a No. 27 Pre-heat Tip on his welding torch to facilitate the bending operation. He had worked 5 to 10 minutes at this task when he began coughing. He climbed out of the chlorinator and remained outside until he had ceased coughing. He then returned inside the chlorinator and resumed heating the coil for bending. He had worked for another 5 to 10 minute period when he began coughing violently and shouted to the other two mechanics who were in attendance at the top of the chlorinator that he could not breathe. He started to climb out and was assisted by the men outside who reached down, grabbing him under the arms, and lifted him from the chlorinator. The injured continued to cough violently and have difficulty with his breathing. He was assisted and/or carried from the upper level to the ground level, placed on a stretcher and transported to the Plant Dispensary. At the dispensary, he was given oxygen for approximately 15 to 20 minutes during which his coughing subsided and his breathing returned to normal. He was also administered an antidote for possible chlorine inhalation. No injury except chest soreness and muscular soreness resulted.

Cause: Examination at the scene of the incident showed that the chlorinator had been properly washed out, and in addition, residual Aroclor had been driven off the inner walls by heating with a gas torch. Statements by several individuals experienced with chlorinator repairs indicated this was one of the cleanest chlorinators they had ever seen. A fire permit issued on 9/14/62 for a period of seven days was attached to the welder's cart on ground level. The signature of the chief operator signified the chlorinator had been field inspected and was okay to be worked on. The nature of work as described on the permit was cutting and welding on #1 Chlorinator. No indication was made of the need for work on the inside of the vessel or the need for a Tank Entry Permit. No Tank Entry Permit had been issued. The bottom side plate was off of the chlorinator but this opening was inaccessible and far too small for exit in case of an emergency. All process and utility lines to the chlorinator were properly disconnected.

It is the Committee's opinion that the injured's torch flame consumed the oxygen in the confined space and produced combustion gases which caused his violent coughing and apparent anoxia. Possibly residual HCl, or decomposition gas products from residual amounts of Aroclor on the walls of the chlorinator contributed to his coughing seizure. The opening in the bottom side of the chlorinator was not capable of furnishing sufficient draft to replace the oxygen content of the air or remove the combustion gases from the welding torch rapidly enough to maintain a safe oxygen level. The accident could have been prevented by the use of a supplemental draft or supply of breathing air from an external source. Proper use and understanding of Fire Permit and Tank Entry Permit check lists, together with the better communications these check lists can afford, would have prevented this incident.

Preventive Measures:

1. A complete review of Tank Entering Permit Procedure and Fire Permit Procedure with emphasis on what constitutes the hazards for which these check lists are formulated.
2. Maintenance and Production to study and revamp coils on chlorinators so that need for entering of these units is eliminated. No spare coils should be procured until revision is complete.

CASE HISTORY NO. 856

Heat Exchanger Undergoing Pressure Test Is Ruptured

Description: On December 14 at 10:15 a.m., two boilermakers were in the process of hydrostatically testing the overhead exchanger when the top cast iron head ruptured; neither man was injured.

This particular exchanger, located on the seventh level of the department, has a design pressure of 115 psig and an operating pressure of approximately 50 psig. The exchanger had been filled with water; but, water was not flowing out of the vents. Examination through the vent connections showed that a full face gasket had been installed on the head flange, forming a barrier between the water in the exchanger and the vents. The boilermakers punched holes through the gasket and continued to fill the exchanger with water. The pressure was raised to 125 psig at which time the top head section ruptured. Pieces of metal were thrown into an adjacent operating area. One boilermaker was standing on the opposite side of the exchanger and was not exposed. The other boilermaker was standing on a structural support and was located about eighteen inches above the handrail on this level. He was soaked with water; but had he been hit with metal or otherwise dislodged from his position, he could have fallen seven stories to the ground.

Cause: An improper procedure was used. The exchanger was not vented properly before pressure was applied. The test pressure was in excess of the normal one and one-half times working pressure. The position of the boilermaker was hazardous.

Preventive Measures:

1. The incident was discussed with the two boilermakers for their suggestions for procedure improvement. These are included in the comments below.
2. Corrosion and Inspection Section will examine the metal on this exchanger (this is an old exchanger and possibly is weaker than the new one) and will review other similar exchangers in this unit to evaluate their physical condition.
3. This incident will be discussed in the various craft safety meetings during January.

Comment: As a guide to future hydrostatic testing of this type of equipment, vent valves should be installed at the highest point on each exchanger, full-face gaskets should not be used on the heads of such exchangers; and as a guide, cast iron equipment should not be tested at more than one and one-half times working pressure.

Editor's Note: The comment at the end of the case history description recommends that cast iron equipment should not be tested at more than 1-1/2 times working pressure. This is not in agreement with the ASME Unfired Pressure Vessel Code which specifies that the test pressure should be 1-1/2 times the designed working pressure.

Generally, vessels are operated at pressures considerably less than the designed working pressure, so it is conceivable that in this case where the operating or working pressure was approximately 50 psig that a test at 1-1/2 times this pressure, which would be 75 psig, might mistakenly be considered as a proper or suitable test. Subsequently, it is entirely possible that an occasion would arise when it is desired to raise the operating pressure and the designed pressure will be considered as the limit. If the vessel, however, has only been pressure tested to 75 lbs. as recommended in this report, the unit could fail in service rather than under hydrostatic tests with consequent potential serious results.

CASE HISTORY NO. 857

Cooling-Tower Fan Breakage

Description: A fan blade in a power house cooling tower broke off while the fan was in use. The 42-pound cast aluminum blade, about 8 feet long, struck and broke the light wooden railing above the tower cone and was thrown off the tower, landing on the ground about 40 feet from the base. Fortunately, no employee was in the path of the blade, even though minutes before the fire brigade had been on the cooling tower and at the time of the incident, were walking along the road near the tower. The vibration switch on the fan shut down the motor following the occurrence. Property damage is estimated at $4,000.

Cause: Corrosion and erosion caused a failure of the torque tube (drive shaft) some 9 inches from the motor coupling. When the tube failed, the loose end was thrust upward and struck the fan blade with sufficient force to break it and give it sufficient upward motion to clear the cone. This blade was one of twelve on the fan.

Preventive Measures: Stainless steel torque tubes will be used to replace galvanized tubes and a third retaining bracket is being added near the center of the tube. In addition to annual and semi-annual inspections by plant and outside agencies, a special inspection is being conducted of all fan drives with particular attention being given to torque tubes.

CASE HISTORY NO. 858

An Explosion Results When Furfuryl Alcohol Is Reacted with Cyanoacetic Acid

An explosion occurred in a laboratory when Cyanoacetic acid was reacted with furfuryl alcohol in an attempt to form the ester, furfuryl cyanoacetate.

The reagents had been mixed and transferred to a one-liter, three-neck flask equipped with a thermometer, stainless steel agitator, and a condenser. Three to four minutes after the agitator was turned on and heat applied, the explosion occurred.

The explosion was of considerable force, and came with no preceding observable rise in temperature of the mixture. A heating mantle holding the flask was slightly deformed by the force with which it was thrust against the ring stand. Part of the glass cloth and glass wool lining were blown out of the heating mantle. The flask was blown to bits, the thermometer and goose neck were broken, but the condenser was undamaged. The inside of the hood was spattered with a solid, dark brown product of the reaction. Small pieces of glass were blown out into the laboratory, causing a slight injury to the forehead of one person in the laboratory.

Very few reference or textbooks give any warning of danger in reacting furfuryl alcohol with acids. Some books do note that furfuryl alcohol is unstable in the presence of strong mineral acids. Organic Syntheses, Collective Volume I, page 285, describes preparation of furfuryl acetate by reacting furfuryl alcohol with acetic anhydride using sodium acetate as a catalyst. There is an appended note indicating that the product can be obtained without the sodium acetate, but there is no warning, anywhere, of danger of explosion in running the reaction.

A further library search seeking to establish the cause of the explosion turned up the statement that furfuryl alcohol reacts with hydrochloric acid with explosive violence, with the formation of a dark brown product. (Marcusson, Berg., 58, 869).

It is concluded after the above-described laboratory explosion that either a strong acid was present as a contaminant, or that cyanoacetic acid is strong enough to cause the violent polymerization of furfuryl alcohol.

Discussion of this incident with other qualified chemists indicates it is not generally known that there is a possibility of violent explosion when furfuryl alcohol is in contact with an acid.

Editor's Note: A writer takes issue with the last paragraph of this case history that "Discussion of this incident with other qualified chemists indicates it is not generally known that there is a possibility of violent explosion when furfuryl alcohol is in contact with an acid."

The precautionary label used on a manufacturer's containers carried in bold face type the words "Reacts violently with strong acids."

The writer also quotes a number of literature references all drawing attention to the "explosive violence" of its reactions with mineral acids or strong organic acids. He concludes that the contributor failed to familiarize himself sufficiently with the behavior of furfuryl alcohol prior to carrying out the "ill-fated" esterification reaction, and that the outcome should serve to emphasize the need to work initially with small quantities when working with unfamiliar materials.

CASE HISTORY NO. 859

Spilled Four Gallons Solvent on Laboratory Floor--Fire!

Description: Ether and hexane had been mixed in equal proportions to a total of four gallons in a 5 gallon pyrex carboy setting on the floor without any protective container. As this bottle was being moved slowly across the floor, it struck against a nearby empty glass carboy and broke, spilling the contents on the floor. One of the two men in the laboratory immediately left to warn the occupants of the adjacent laboratory. A Laboratory Service Man came into the laboratory at this moment and was sent for a bucket and mop. He had returned and had mopped up a considerable amount of the spilled solvent into the bucket, when the vapors were ignited. There was no strong explosion, although the concussion was felt for a considerable distance in the building.

Both men who were in the laboratory escaped with only minor burns, although one man had the bottoms of his trouser legs burned off.

Because of the thick smoke which developed from the ensuing secondary fires, the entire laboratory area was evacuated. Secondary fires started in the space between the backs of the center bench cabinets and in trash containers. Five automatic sprinkler heads opened and held the fires in check. The plant fire brigade, backed up by the community fire department, completed extinguishment.

Cause: The source of ignition is believed to have been one of several muffle furnaces operating in excess of 1,000°C. in the adjacent laboratory. This was indicated by scorch marks on cabinets facing the furnaces in the adjacent laboratory. There was no evidence of any sustained fire in that laboratory. This is borne out by reports of the occupants of the laboratory.

It is believed that the solvent vapors travelled from the laboratory where the spillage occurred into the adjacent laboratory through any one of a number of openings in the common wall. It has been demonstrated that this is the normal direction of air flow between these laboratories.

Preventive Measures: Immediate:

1. Protective containers will be used for all glass bottles larger than 5 liter size in which flammable solvents are being used, stored or handled.
2. The muffle furnaces in the adjacent laboratory were shut down pending further investigation.

Long Range Measures: A more suitable location for research work involving muffle furnaces is being sought. In the meantime, this laboratory is being provided with an auxiliary air supply to keep it positive in respect to the adjoining organic laboratories.

Efforts are also being made to provide more suitable space for large-scale column chromatography and other semi-commercial operations. At the present time, much of this work is done in a two-man, small-scale organic research laboratory.

CASE HISTORY NO. 860

Safety Training Prevents Injury from Electrical Switch Explosion

An AEC contractor employee was saved from certain injury by following safety training received in the operation of electrical switches. Using his left hand to throw the switch, he was positioned at the side, instead of in front, of the switch mechanism when it exploded. Following are pertinent details of the accident as reported by the contractor:

Description: An operator energized the control circuit and then turned on the operating switch for an air compressor, which, for reasons detailed below, caused an adjacent mercury over-temperature control switch to explode. No personnel injuries were sustained.

Investigation revealed the following facts:

1. The compressor had been shut down for replacement of the cooling water valve and was being restarted.
2. The operator activating the switch did so with his left hand, thus positioning himself to the side of the operating switch and the mercury over-temperature switch.
3. As the operating switch was activated, the mercury over-temperature switch exploded, blowing the switch cover and mercury approximately 15 feet past the operator.
4. The operator immediately de-energized the compressor control and locked out the power supply.
5. Subsequent to the incident, the mercury spill was cleaned up.
6. Investigation revealed that the insulation inside the operating switch had failed, allowing 400 volts to short to ground through the operating switch cover and permitting excessive current to flow

through the mercury over-temperature switch.

7. The mercury inside the mercury switch apparently vaporized due to the excessive current and caused the explosion.

8. The repair work performed on the air compressor prior to the incident did not involve any of the control components that later failed.

Cause: This incident was apparently caused by repeated use and wear of the control switch.

Recommendations: 1. Re-emphasize to personnel the importance of standing to the side of switchgear which they are energizing, as was done in this incident.

2. Convert control circuitry and components to 110-volt operation, where feasible, to reduce the possibility of such incidents.

CASE HISTORY NO. 861

Open Kettles--Splash Hazard

Description: The employee was loading copper wire into the top of a partially open 5 x 5 foot chlorinator. The chlorinator contained an acidic solution of cuprous ammonium chloride up to a level about six to eight inches from the top. He used a five-foot 2 x 4 to push the wire to the rear of the chlorinator. During this pushing operation, the 2 x 4 slipped from the employee's gloved hands and fell into the solution. The solution splashed into his left eye resulting in a severe chemical burn.
(Note: The employee was wearing safety glasses with side shields – a department standard.)

Cause: 1. The design of the chlorinator was thought to be adequate for the loading operation. This operation has been performed without serious incident for thirty years.

2. The 2 x 4 push stick slipped from the employee's hands. This might have been caused for two reasons: (1) the push stick was not properly designed, (2) the push stick and/or gloves might have been wet with the solution.

Preventive Measures: 1. An adequate (nitrometer type) face shield will be required on this job. Supervision is making a survey of all department operations to find if more adequate eye protection is required on other jobs.

2. A properly designed push stick will be provided on the job.

3. Supervision has requested a study from the Engineering Department to modify the chlorinator to reduce the splashing hazard during the loading operation.

4. Supervision of Organic Chemicals Department will devote more effort to improving operating procedures, equipment, and instructions on all jobs in the department.

CASE HISTORY NO. 862

Unsafe Arrangement for Loading Semi-Trailer

Description: A Yale Transporter was being used to load a trailer with bags of sodium sulphate. The floor of the trailer was 9 inches higher than the loading dock. Because of this difference in height, the dock plate was sharply inclined. As the loaded transporter was backed into the trailer, it would hang up on the dock plate. A fork truck was being used to raise the front or battery end of the transporter and push it back off the plate into the trailer. The injured employee grasped the handle of the transporter to lower it to operation position. As he did, the transporter slipped off the fork on the right side causing the end of the fork to fly up and strike the injured employee's right hand and resulting in laceration and contusion of the right middle finger.

Cause: Unsafe Act – Using equipment unsafely: (1) Use of transporter on the dock plate and using fork truck to dislodge transporter. (2) Improper body position—injured should not have placed himself in exposed position, and served no useful purpose in so doing.

Unsafe Condition: Hazardous arrangement – trailer was too high for loading dock and magnesium dock plate used did not fit properly.

Supervisory Responsibility: Responsibility for safe work conditions, safe work practices and providing correct equipment. Supervision not only must detect hazards and either eliminate or safeguard, but also must follow up to insure that safe procedures always are followed.

Preventive Measures: 1. Trailers that do not match up safely with the loading platform will not be loaded at this dock and will be rejected unless they can be loaded elsewhere in the plant, as for example in a roadway by a fork truck lifting load to truck bed.

2. Transporters will not be used to load trailers in instances where the transporter will hand up on the dock plate. Purchase of different type of dock plate under consideration.

CASE HISTORY NO. 863

Molten Sulfur Overflows from Tank Car

Description: A tank car of molten sulphur was placed on the railroad siding near the unloading station. The steam and condensate lines were connected to the car to heat the sulphur prior to unloading. The car was unattended during the heating cycle.

During the heating cycle the sulphur in the car expanded, part of the contents overflowed to the ground. There were indications from sulphur on a nearby elevated catwalk, that prior to overflow there was an encrustation that formed over the liquid sulphur and when this allowed release of pressure, sulphur sprayed from the dome of the car. The remainder of the loss seems to have been from a bubbling overflow of the car. Approximately one half of the contents was overflowed to the ground.

Cause: An investigation revealed a leaking coil in the heater which allowed steam to enter the car.

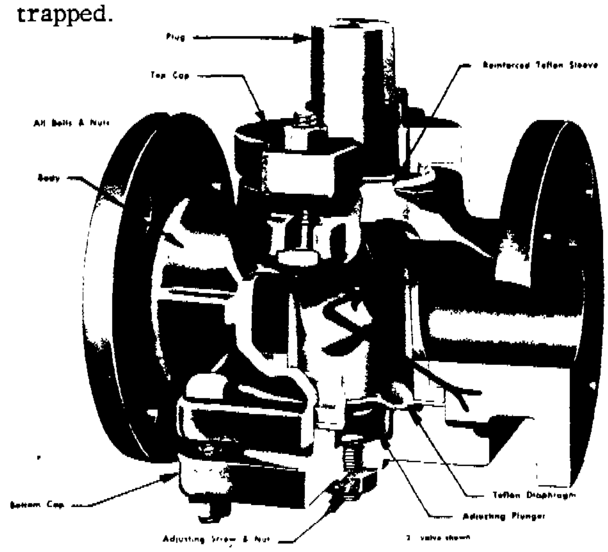
Preventive Measures: The supplier has been contacted concerning the inspection and testing of all cars.

This occurrence was discussed with all sulphur unloading personnel.

CASE HISTORY NO. 864

Valves Can Be Pressure Traps

Description: A valve taken off the line is not necessarily free of entrained liquid under pressure within the valve, and such a condition is particularly true of plug cocks. An internal view of a plug cock is reproduced below, with the large arrow in the center indicating the area where acid, or other hazardous material can be trapped.



Cause: Here are two cases in point:

1. Recently, an employee wearing full protective clothing removed a screwed-type plug cock from an HF line. He put the cock down on a grating covered trench, left the area, and removed his protective clothing. When he returned a few minutes later, he held the cock down with his foot, while he opened it. HF and other material spurted out, striking him in the face. Safety glasses with side shields, his only protection, saved him from almost certain blindness, but his face was covered with numerous pitted burns, requiring extensive injections of calcium gluconate.

2. Some years ago at another location, an employee was cleaning and greasing several plug cocks which had been out of service for about six weeks. Cocks were being washed with solvent and then greased. Employee opened one of the cocks after greasing and was sprayed on both forearms with HF. Two hospitalizations were required, the second for skin grafting, and employee was under medical attention for about a year.

Preventive Measures: To prevent such injuries, the following precautions must be followed:

1. When removing a valve or plug cock, screwed or flanged type, from a line, full protective clothing, including a face shield, must be worn until the valve or cock has been opened, drained, washed and decontaminated.

2. Valves and plug cocks should be opened on the line before removing them. This may relieve built-up pressure, but there is no guarantee it will.

3. No plug cock that has been removed from a line is to be left unopened for any period of time.

Note: Valves and plug cocks may be opened under water as an additional precaution.

Editor's Note: (a) The note following this case history indicates that valves and plug cocks may be opened under water as an additional precaution. This procedure would not be suitable in dealing with all liquids for several examples could be given where materials and water react in such a manner that would make the suggested practice a hazardous one.

(b) "As a modification of our valves we can supply the plug with a 1/8 in. drilled vent hole in the plug. This hole is drilled in the side of the plug through to the plug port. When the plug is in the closed position the liquid then entrapped in the plug port can drain or at least relieve the pressure of the liquid entrapped. This feature is most commonly utilized on liquid chlorine or other liquefied gas services. We have never had a request nor have we experienced problems such as you describe on HF service. In any case, this 'vented plug' could be utilized." The manufacturer's name can be provided on request.

CASE HISTORY NO. 865

Liquid Oxygen Pump and Piping Explosion

Description: An explosion occurred, after a deriming operation and during the startup period of an oxygen column, in the impeller section of a liquid oxygen pump and in the inlet and outlet liquid lines and the vapor vent line, killing one man and injuring three others. Following the explosion, a fire occurred at the refrigerating unit (halogenated hydrocarbon) three feet away involving a mixture of the refrigerant and oil. Since the inlet valve to the pump was bent so that the oxygen escaping from the column could not be shut off immediately, it took about fifteen minutes before the local foreman could extinguish the fire. Damage was confined to the pump, piping, and refrigerating unit.

Cause: The explosion apparently involved oil accumulations in the base of the pump impeller casing sump and in horizontally installed bellows type flexible hose lines leading to and from the liquid oxygen reflux pump. The source of ignition is not known although the explosion occurred during or immediately after the slow opening of the inlet valve introducing liquid oxygen into the warm pump.

Preventive Measures:

1. Drains will be installed in the bases of the impeller casings.
2. Increased efforts will be made to keep oil from being introduced into the air or oxygen stream and to remove it more efficiently wherever it is introduced.
3. All new flexible hoses will be installed with axes vertical.
4. Present pumping equipment will be modified, at least temporarily, to provide cooling and inerting with LQN before starting up or repairing.

CASE HISTORY NO. 866

Lack of Oxygen

Description: The employee was preparing to check for contamination on an agitator shaft in a 3,500 gallon reactor. After placing the ladder in the reactor, he put on the safety belt and life line. As he descended into the reactor, he smelled styrene fumes and asked the standby operator to bring the air hose to the reactor. When the standby operator returned to the reactor, he saw the operator lying on the bottom of the reactor. (The standby operator quickly dropped the air hose into the reactor with the air stream flowing over the man's head. He then summoned help and the man was removed from the reactor, under his own power.)

Cause:

1. There is a possibility of contamination on the agitator shaft when the seal on the top of the agitator has been replaced.
2. The material in the reactor had just been removed by nitrogen pressure, leaving a nitrogen atmosphere.
3. The vessel entry procedure was not followed because the job was of short duration and the man was in a hurry to get equipment back into operation.

Preventive Measures:

1. Supervision will review, with all employees, the vessel entry procedure. It will point out the necessity for a complete follow through even on jobs of short duration.

CASE HISTORY NO. 867

Excessive Pressure Results from Overcharging Reactor

Description: At about 6:50 a.m. a 770 gallon reactor in the pilot plant got out of control and resulted in excessive temperature and pressure within the reactor. The building was evacuated; but, there was no injury or damage to the equipment.

This batch reactor was started up at about 5:40 a.m. Immediately upon catalyst addition, temperature and pressure began to increase and, following normal procedure, venting of the reactor was started to slow down the reaction. Venting was slow and difficult due to carry-over of liquids and solids from the reactor to the 1 in. and 2 in. vent lines. Pressure control, previously set at 500 psi, was achieved; but the temperature continued to increase, necessitating continued venting. At about 6:45 a.m., the agitator stopped due to an overload. The vent lines then plugged and pressure increased very rapidly. When the pressure reached 600 psi at a temperature of 90°C., the building was evacuated and the emergency alarm sounded. At about 7:20 a.m., the building was reentered, and it was found that the pressure had peaked at 750 psi, then had decreased to

330 psi and leveled out. This is a self-limiting system in that as temperature and pressure increase, reaction rate increases, but as reactants are used up, the pressure then decreases. The vessel was designed for an operating pressure of 660 psi at 163°C. The vessel is equipped with an emergency relief valve set at 750 psi which was plugged as a result of this incident.

Cause: An overcharge to the reactor of approximately 120 gallons was made. This, in turn, caused poor agitation, poor heat transfer and loss of temperature control. As attempts were made to vent the reactor, slurry was blown into the vent lines and these eventually plugged.

There are two possible sources of error which could have caused the overcharge:

1. Residual slurry left from the previous reaction since there is no method of determining if material is left in the reactor.

2. Metering errors in measuring the raw material charged. This is the more probable cause since the overcharge checked very well with the error in the meter found later.

Preventive Measures:

1. The meter calibration was checked and a measuring tank is now being used for adding charge to the reactor.

2. Other liquid level detection methods will be studied.

3. An emergency system, independent of normal vent system, will be designed.

4. The possibility that residual polymer could initiate reaction at an abnormally high rate will be checked.

CASE HISTORY NO. 868

Over-Exposure to Chlorine

Description: During start-up, an operator opened a valve in a chlorine feed line which releases liquid chlorine into the reactor. This caused an excessive amount of chlorine in the system which vented to a water seal pot off the recycle tank near the operator, and he inhaled vapor while closing the valve.

Cause: The excess chlorine in the line caused the accident. Operating Procedure called for opening the chlorine valve last during start-up. The vent line froze up causing chlorine to vent through the water seal pot. The operator was not wearing a gas mask.

Preventive Measures: Vent line will be removed from sewer and tied to recycle tank vent, then to caustic scrubber instead of water seal pot, so that chlorine will be neutralized. Operating procedure has been changed so that chlorine valve will be opened first when starting up. Operators have been instructed by the Area Superintendent to wear gas masks during start-up.

CASE HISTORY NO. 869

Unsafe Steam Line Connections

Description: A 5-foot diameter, 20-foot long steel tank fastened on a highway trailer is used for transporting neutral liquor and as a storage tank in a manufacturing area. The temperature of the liquor is maintained by a bayonet heater with steam (at 15 psig) supplied through a 1-inch I.D. steam hose with a Westinghouse connection. Just after the steam supply had been connected the operator noticed there was no condensate being discharged from the steam trap, indicating a frozen line. He closed the steam supply valve but did not break the Westinghouse connection, since pressure had built up in the heater and there was no bleed valve. He started around the end of the trailer to get another steam hose to thaw the frozen line and tripped on the connected hose in a narrow space, losing his balance. His hand struck this hose with sufficient force to disengage the Westinghouse connection. Steam and hot condensate sprayed onto his back, left side and arm.

Cause: Westinghouse connections inadequate for steam.

Preventive Measures: Westinghouse connections have been replaced with Standard Boss couplings (twist-lock) on steam connections and bleeder lines have been installed on each neutral liquor trailer.

CASE HISTORY NO. 870

Overheated Wax Ignited Spontaneously

Description: A sales trainee in Development Laboratory with only three weeks experience on work assignment, had been carrying out coating trials with a resin and paraffin wax blend. He had melted the blend in a stainless steel beaker about mid-morning and had put the beaker with the unused part of blend back on the hot plate to keep it molten. When he returned to the area about mid-afternoon, he noticed that the blend was smoking on the hot plate. After turning off the hot plate, he carried the beaker across the area to a 50 gallon pail used as a receptacle for waste wax. As he started to pour the blend into the pail, a flash fire started. When he dropped the beaker a fire occurred in the pail, in the beaker, and in a few spots of dropped wax in between. Some of the wax had also spilled on his clothing and ignited. He sustained burns on both hands, abdomen, and right thigh and arm.

Cause: The wax blend had been allowed to heat above its auto-ignition temperature. The fire did not start until the blend was poured, because the surface was covered by gaseous decomposition products which were relatively cool.

Preventive Measures: Better safety training will be given new employees and controlled-temperature equipment will be used for wax-blend storage.

CASE HISTORY NO. 871

Overheating of Tank Car of Rosin Results in Overflow

Description: A rosin size tank car was hooked up to the car and was placed on automatic control. The automatic control consists of a Mercoid temperature controller in the tank car which controls a solenoid valve on the steam line feeding the tank car coils. The temperature of the car rose to 180°F. by about 6 p.m. and was still at 180°F. when the plant was closed up for the evening at 10 p.m. At 2:45 a.m. the next morning, the plant superintendent was notified that a tank car was running over. Inspection by the superintendent at 2:55 a.m. confirmed this. The temperature of the car at this time was 212°F. The solenoid valve was still open, feeding steam to the coils.

Cause: Up until at least 10 p.m. the automatic control system had worked perfectly as it had done on the previous eleven tank cars heated by this same procedure. The normally closed (fail safe) solenoid valve stuck open despite the fact the current to the coil was off. After manually turning the current off and on again and removing the steam pressure from the valve, the solenoid valve returned to normal operation.

Preventive Measures:

1. The solenoid valve has been replaced.
2. A preventive maintenance schedule has been set up for internal inspection and cleaning of the solenoid valve every 3 months.
3. A complete unloading operating procedure has been written.
4. In addition to detailing the current procedure, a section has been included for pretesting the automatic control system at 140°F. prior to setting it up to 180°F., the normal holding temperature.
5. The tank car heating will not be done overnight, over weekends, or holidays when no one is present.

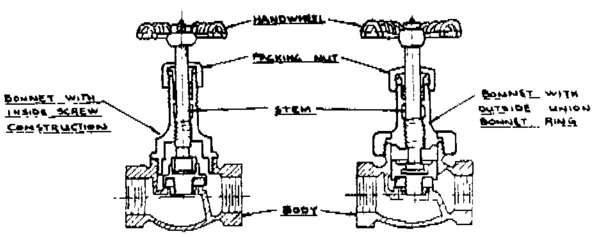
CASE HISTORY NO. 872

Valve Bonnet Blows Off Steam Valve

Description: The bonnet of a Figure 200 2-in. OLC globe valve blew off and narrowly missed striking a mechanic who was in the process of closing this valve. The valve is located in a branch take-off from the main 125-pound steam line approximately 15 feet above the second floor. The valve bonnet, stem and handwheel assembly weighing four pounds projected horizontally a distance of 20 feet before striking a water line with such force that a 2 in. nipple connection was broken in the water line.

The branch shut-off valve was being closed and tagged as preparation for a maintenance job. The mechanic was working from a straight ladder and was in position 15 feet above floor level. At the time of the incident the mechanic's head was below the valve as he was reaching up with both hands to perform the final closing. Although he received first degree steam burns on both wrists, the mechanic descended the ladder safely.

Cause: This valve is an old design having internal threads in the valve body for holding the bonnet in place. Examination after failure disclosed that the bonnet threads were worn or corroded permitting the bonnet to slip out of position. Plant engineering practice has revised specifications to use an outside union bonnet design valve for steam service up to 125 psi. (See sketch)



OIC FIG. 200 OLD TYPE

OIC FIG. 520 NEW TYPE

Preventive Measures: To prevent similar incidents, the following steps are being taken:

1. A program will be started to replace all pressure valves of this type with the preferred outside union bonnet type. This

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program will be initiated with immediate replacement of all frequently operated valves of this type in 125-pound steam service.

2. The incident is being reviewed with maintenance and production groups in order to re-emphasize the proper body position when operating high pressure valves.

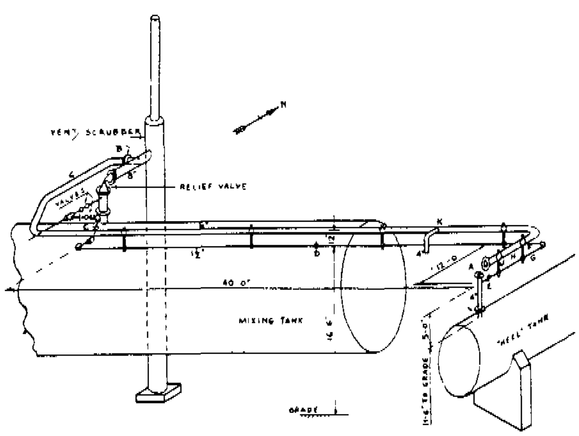
Editor's Note: "The preventive measures state that valves with inside screw construction will be replaced with an outside union bonnet design valve. For positive protection we would recommend valves with bolted bonnets."

CASE HISTORY NO. 873

Detonation--Tried to Flame-cut Pipe Containing Plug of Impure Ammonium Nitrate

Description: At 11:05 a.m., an explosion occurred in a section of 1-1/2 inch pipe which was being taken down from its position above a horizontally mounted tank in the nitrogen solution manufacturing area. Fragments of the exploding pipe, and possibly the force of the exploding pipe, and possibly the force of the explosion itself, produced injuries which were instantly fatal to a pipefitter. A welder, who was on the opposite side of the pipe, received a permanent partial disability due to facial disfigurement. The accident occurred during the preparation for the production of a new product at the plant. Plans for this production included utilization of a horizontally mounted steel tank which had formerly been used as a "heel" tank in nitrogen solution manufacture. This tank had been out of service for about a year. It had various liquid and gas piping connections, the pertinent ones of which are shown on the sketch.

On the Friday preceding the accident the pipefitter asked for a permit to burn and weld on the 6-inch relief line between the heel tank and the vent scrubber. Referring to the sketch, the plans



call for a 4 inch connection to be welded into this line at point 'K'. The line was open at one end since the relief valve at point 'A' had been removed. He was told that it would be necessary to break the line at point 'B', so that it could be flushed with water, before a permit would be given. He then asked if it was permissible to burn off the bolts of the joint at point 'B', since they were frozen and the nuts could not be threaded off. This was not permitted, and he was required to open the joint at point 'B' by mechanical means. The line was then washed out with water and the permit given.

Also on this same day, the pipefitter broke the union in the 1-1/2 inch equalizing line which ran parallel to the 6 inch relief line about 1 foot lower, at point 'E'. It should be stated that this line had been disconnected for some months at point 'C', where a union had been opened. Prior to this the pipefitter had asked if the 1-1/2 inch equalizing line would remain when the construction project was finished. This line had no part in the project and does not appear on the drawings or work instructions. He was told that the line was not part of the project and should be removed. There was no discussion of when it should be removed or whether it was safe to work on.

On the day of the accident (Monday), the pipefitter informed his supervisor that he needed a permit "to finish the work I didn't complete Friday". This referred to the 4 inch connection at point 'K'. The permit was granted on the basis that the pipefitter was to resume work on the same line that he had worked on Friday. The line was again flushed with water before the permit was countersigned. However, the wording on the permit was not changed to read that the pipefitter had permission to weld and burn on "construction for production of new product", obviously a much broader permission than previously given.

At 10:45 a.m. the pipefitter discussed with his Foreman the near completion of the work that they started on Friday. They then discussed new material which was to be brought to the job site after lunch. A list of materials was made up of equipment necessary to start the new job.

Cause: The welder states that after completing work on the tie-in to the 6 inch relief line the pipefitter said "let's get this 1-1/2 inch line down". Standing on the top of the heel tank, the bolts securing the pipe hangers at points 'J' and 'H' were burned loose. Since the union was disconnected at point 'E', this left about a 12 foot length of the 1-1/2 inch pipe unsupported at the south end. The pipefitter instructed the welder to burn the pipe in two at point 'F'. The pipefitter was standing on the heel tank facing west and supporting the pipe in the crook of both elbows. As the welder applied his torch at point 'F', the explosion occurred immediately, before the torch had actually burned into the pipe. The center of the explosion seems to have been at about point 'G' and it propagated in a southerly direction toward point 'E'. The pipe at point 'F' was not ruptured. There was about 4 feet of line left unruptured north of point 'E'. Although the pipe was empty at point 'E' when the pipefitter looked into it, it was plugged solid some 2 feet north of this. The plugging material analyzed 58% ammonium nitrate, 34% iron oxide, 4% urea, and 0.1% oil. The force of the explosion fractured the line adjacent to the union at point 'D'. The line was plugged solid at this point and the material analyzed 32% ammonium nitrate, 55% iron oxide, 3.2% urea, and 0.6% oil.

The immediate cause of the explosion was the detonation of confined, contaminated ammonium nitrate set off by the heat of the welder's torch.

Preventive Measures:

1. The forms pertaining to the issuance of burning and welding permits, will be reissued and brought up to date. A study will be made of the present form for improvement of language and definition of the work covered.
2. Working through the General Safety Committee and the Subdivision Safety Committee, a plantwide effort will be made to make the permit procedure more careful and more effective. Closer and more specific descriptions of work covered will be required. All employees issuing and receiving permits will be re-educated as to the need for a tight and rigorous execution of the permit procedure.
3. Certain other safety regulations related to the permit procedure will be re-examined and tightened as necessary. Our safety education effort will be intensified in these related areas as necessary.
4. Maintenance supervision will review carefully the extent of the authority which is delegated to maintenance craftsmen, particularly where this delegation involves the exercise of judgment by the hourly employees as to to whether or not properly safe conditions exist.
5. Working through the General Safety Committee, an effort will be made to revitalize the overall plant safety effort, to create new interest in safety and an improved plant consciousness of safety as a way of life.

CASE HISTORY NO. 874

Shock Sensitive Contaminent Detonates Inside Shaft Bearing

Description: Two employees were preparing to remove a bearing assembly from a shaft. The bearing was part of a sodium bromate crusher that had been transferred from the Bromide Plant to the Machine Shop for repair. The pillow block bearing had been degreased at approximately 255°F., removed from the degreaser and placed on the floor. One machinist, using a lead hammer, tapped the bearing sleeve on the shaft. There was an internal explosion shattering the bearing assembly into multiple pieces. Three employees were injured; two machinists and a nearby crane operator. One employee sustained fatal injuries. One was hospitalized with severe injuries and the third hospitalized with less serious injuries.

Cause:

1. The pillow block bearing apparently was contaminated with sodium bromate that may have been carried into the bearing during service, water washing, or solvent degreasing.
2. The bearing was lubricated with a petroleum base grease that contributed to the formation of an unstable compound in the internal parts of the bearing.
3. The bearing was placed in a vapor phase degreaser elevating the temperature to approximately 255°F. The degreasing may have concentrated the chemicals in the bearing.
4. Shock to the outer surface of the bearing may have initiated the reaction of unstable compound.

Preventive Measures:

1. Hal-O grease (chloro tri fluoro ethylene polymer) will now be used to lubricate the bearings on the crusher unit. Petroleum base lubricants will not be used.
2. The department will continue to replace all bearings with new bearings when maintenance work is required on the crusher.
3. The Bromide Department and Maintenance Services Department will maintain complete communications to perform safe work.
4. Engineering & Construction Department has been assigned the job of searching for an improved method of crushing bromate. Any improved method will be considered for installation.
5. A study will be conducted by the Bromide Plant to determine any potential hazards in equipment or processes that may be caused by the presence of incompatible chemicals.

6. It is recommended that all plant departments carefully examine all equipment or processes involving unstable chemical materials.

7. A task force has been appointed under the jurisdiction of the Engineering Department to assist plant departments in evaluation and correction of hazards related to unstable chemicals.

CASE HISTORY NO. 875

Sight Glass Burst When System Was Pressurized

Description: The employee was attempting to transfer polymer slurry from a 3,500 gallon reactor to the north blow-down tank. The kettle pressure of 80 psi is used to transfer the material. With the valve of the transfer line to the south blow-down tank closed, the transfer was started. The 4-inch diameter bull's-eye sight glass on the transfer line to the south blow-down tank blew out suddenly. The polymer slurry and broken glass struck the employee on the right side of the head, which resulted in a moderate cut to the right ear.

Cause:

1. The sight glass is located on the pressure side of the valve, which caused an 80 psi static pressure on the sight glass.
2. Unaware that 80 psi would break the sight glass, since it is rated at 190 psi.
3. It is very possible that the sight glass had a scratch on its surface which caused it to fail at a lower pressure.

Preventive Measures:

1. As a temporary measure, a wire mesh guard will be installed over the sight glass.
2. The shut-off valve on the transfer line will be relocated to be ahead of the sight glass.
3. Work with the glass company to determine why the sight glass failed, and what can be done to prevent the recurrence of the incident.
4. Check with other groups to determine if there is a safer piece of equipment to do the job.

CASE HISTORY NO. 876

Static Ignites Ligroin in Centrifuge

Description: A fire occurred when a static charge built up in a centrifuge and discharged within a vapor rich atmosphere.

A centrifuge operator was looking into the basket of the centrifugal extractor into which the slurry of ligroin and crystals was being fed by gravity from the reaction vessel. A flash occurred which burned the operator's face and hand. The fire which ensued enveloped the equipment and also discharged into the floor drains surrounding other chemicals in the area with flames.

Cause: Static charges are generated whenever liquids are broken up into droplets, fine streams or mists. As they leave the container they carry a charge, leaving an equal and opposite charge on the container. If the container is not grounded the charge may build up to a high degree and when conditions are right a spark occurs. If the spark is within a flammable atmosphere ignition results.

After the fire the centrifuge was checked for grounding and bonding. It was discovered that the resistance between the basket and ground was greater than 15 megohms. It is thought that the grease on the bearings was a sufficient barrier to prevent adequate drainage of the static charge and that the bolts in the framework were near enough to the basket to provide a point for the discharge of the static in the form of a spark. It is also a remote possibility that the mist could have created a charge on some insulated portion of the vent duct which then discharged and ignited vapors which flashed back to the centrifuge.

Preventive Measures:

1. Frequent checks should be made on equipment handling flammable liquids to be sure all parts are adequately grounded. This should include the equipment, pumps, pipelines, hoses, ductwork, etc. This practice should be followed more frequently during winter months because the air within the buildings is dry preventing drainage of static easily through the thin film of moisture which forms on equipment. (Recall the static shocks you receive at home when you touch the door knob or light switch after walking across a rug or waxed floor. This happens less frequently during summer months when the humidity is normally higher.)
2. All parts of machines and equipment such as rolls, rotors, drums, etc. which run in bearings should be looked upon with suspicion that they can be isolated from ground by the grease on the bearings. (The use of conductive grease would contain graphite

and would act more like an abrasive at the high speeds of centrifuges.)

3. Each fall grounding techniques should be reviewed with operating personnel, as a reminder prior to the dry winter months.

4. Gravity flow of flammable liquids is hazardous. An emergency means of shutting off the flow should be installed whether it be remotely operated valves, self-closing valves under fire conditions, or by pumping liquids.

CASE HISTORY NO. 877

Hot Liquid Softens Thermo-Plastic Pipe

An engineer was burned when a plastic pipe separated and sprayed hot (170°F.) alum onto his leg. The alum was being pumped through a two-inch polyvinyl chloride line under pressure at 25 psi. The pipe was rated for 75 psi at 150°F. Swelling of the pipe, couplings and fittings had been observed and a study was made during December to replace it with stainless steel.

The accident points out lessons which should be passed on for the safety of others:

1. Not all plastics are suitable for wide ranges of temperature. Beyond certain temperatures some become soft rather rapidly and lose their strength, others become brittle when cold. Some trade name plastics are produced in a wide variety of "types" with different properties. Therefore, in selecting a plastic by trade name one should be certain that the one selected meets the specifications desired.

2. When there are signs that equipment may fail, shut it down and repair or replace it before an accident occurs.

CASE HISTORY NO. 878

Molten Sodium Metal Overflows from Tank Car

Description: An operator had rodded a tank car of molten sodium and found that one of the drop legs was plugged. He disconnected the quick coupling on the nitrogen supply line at the tank car but neglected to vent the nitrogen pressure (3 psig) already in the tank. When the plug broke loose, sodium spurted six feet in the air, immediately ignited and continued to flow out of the car. Approximately 3,000 pounds of sodium were finally involved. The operator was wearing a fire retardant canvas hood and leather gloves and escaped unharmed to sound the alarm.

The fire brigade responded, cut the electrical power and nitrogen supply to the building. It was decided not to fight the fire due to the hazard to personnel and the fact that the fire fighting effectiveness would be questionable with the sodium continuing to flow. The fire lasted 2-1/2 hours and severely damaged two tank cars and the shed enclosing the area. A light blowing rain at the time of the incident may have contributed to the severity of the fire. Fumes caused the shutdown of several plant operations and the evacuation of nearby trailer homes. Soda ash was used to extinguish the final stages of the fire.

Cause: Several deviations from good practice were the cause of this incident. The nitrogen pressure had not been vented from the tank car prior to the rodding, nor had the circulating oil pump been shut down. In addition, the operator notified supervision of his intentions to rod the car but failed to wait for his arrival or for the arrival of a standby operator.

Preventive Measures: This incident is a good example of the consequences that can result from not following prescribed operating procedures. The need to follow these procedures has been firmly impressed upon operators.

Proposed physical changes include the reduction of the nitrogen pressure on the sodium scale tank and the installation of a separate vent system through the vent valve inspection port on each tank car. The possible installation of a fixed extinguishing system for tank car domes is being studied.

CASE HISTORY NO. 879

Tank Rupture and Explosion of Propane Gas

Description: 6876 gallons of propane gas were being transported as liquid under pressure in a frameless type MC-330 tank trailer. The tank vehicle ruptured and its cargo of propane exploded, resulting in 10 deaths and 17 injuries. Property damage was estimated to exceed $200,000. Nine dwellings, one church, one garage, one house trailer, six outbuildings, two school buses, four trucks and five passenger vehicles were totally destroyed and two other houses were damaged. The accident occurred on a county highway approximately 560 feet northeast of the center of a town. The grade of road at the fatal curve was estimated at approximately 11%; the grade from the point of the curve sign around the curve was approximately 10% descending; the curve itself estimated to be more than a 70° curve. It appears that the vehicle tipped, or was at least partially out of control just prior to the rupture. The cargo tank had a capacity of 8532 gallons. The tractor trailer unit was over 45 feet in length, and, as loaded, had a gross weight in excess of 60,000 pounds. The trailer had never been in an accident.

Cause: Failure of a specification MC-330 cargo tank vehicle. Metallographic examination of ten sample sections cut from points on the weld where fracturing had occurred and of so-called "mating samples" (samples directly adjacent to those ten cut from the tank) showed a number of "undesirable features" in the welding of the cylindrical shell and hemispherical head. One of the samples showed a clear undercut which would create an area of stress concentration. The convexity of the weld in most of the samples appeared to be more than the Code allows. The Code specifies that in steel plate up to 1/4 inch in thickness, the weld build-up shall not be more than 1/16 of an inch. The samples show build-ups as great as 3/16 of an inch. Such excess weld causes a focal point and the tensile stress transferred to the shell by the pressure of the contained gas will therefore not be uniform. One section shows a considerable misalignment between the shell and the head. The Code provides that in plate up to 1/4-inch thickness, the misalignment should not be more than 1/16 inch. Misalignment shown in the sample is 7/64 of an inch. Such misalignment not only causes undue stress but also a bending moment increasing the possibility of fracture. Chamfering of the 1/2-inch plate of the cylindrical part of the tank was insufficient in all cases to reduce its thickness to that of the thinner plate, and in addition, was done by a heat process which altered the structure of the metal, making it more brittle so that any strain would tend to crack it rather than to merely deform it (the hardness was nearly doubled by this process). Pressure exerted by the gas against the very front of the tank is only half as great as the pressure exerted on the cylindrical portion of the tank. The sharp turning of the vehicle back to the right side of the road at the bottom of the hill may have applied an additional stress factor to the weld in question. In addition to the above, evidence obtained during the investigation of this accident supports the conclusion that neither the condition of the vehicle driver, the vehicle, nor the driving of the motor vehicle contributed to the accident, except to the extent that the motion of the vehicle negotiating the curve contributed to the stress on the front girth weld.

Preventive Measures:

1. Inspection by ICC of tanks of this particular model presently in service throughout the country to insure that they do not constitute a threat to public safety.

2. Recommend that regulation be promulgated requiring manufacturers of specification MC-330 pressure tank vehicles for transportation of explosives to file the data and certificate of compliance for such tank vehicles with the ICC, and that ICC register each vehicle and maintain record of its manufacture, major repairs, accidents, and transfers of ownership, which the carrier will be required to report to the ICC.

3. Consideration given to both more frequent and more modern testing specifications. During investigation of this accident, it was brought out that the ASME Code (ICC regulations require specification MC-330 cargo tanks be built in conformity with this Code) is a Code for stationary pressure vessels. It is possible that over the course of years since its manufacture, this tank was subjected to such external stresses and that they cumulatively contributed to its final weakness. Also, frameless vehicles, where the tank itself must absorb such external stresses, are as a general rule undesirable. It is recognized that regulations provide that such frameless tanks must be so constructed that the force of such stresses will be safely absorbed or dispersed, but it may be that such vehicles should not be approved at all. It is also noted that the hydrostatic retest required every five years by terms of present regulations is actually destructive in nature and may (although not shown to have done so in this accident) actually weaken pressure tanks.

4. The proper specifications and the desirability of frameless tanks are matters for careful study and for the gathering of much more expert and technical information. Recommend that proceeding be instituted, looking toward revision of standards for pressure cargo tank vehicles and, specifically, the consideration of the question of whether frameless cargo tank vehicles should be prohibited from transporting explosives.

5. Recommend new regulation be adopted requiring motor common carriers of explosives to specifically route each shipment of explosives from origin to destination. (Different routing would not have prevented this accident; however, it is considered that motor common carriers of explosives must exercise a higher degree of care toward the public than must other transporters.) ASESB Report

CASE HISTORY NO. 880

Chemical Fire

Ten kilos of an azido compound were being prepared. Smaller quantities had been previously prepared and no difficulties experienced.

No difficulty was experienced in the chemical preparation of the material in methyl alcohol suspension. The material was finally dried in a tray dryer heated by an ordinary steam radiator. It was left overnight in the tray dryer in the laboratory where it had been prepared.

During the night, while no one was in the laboratory, the material ignited. There was a puff or mild explosion sufficient in force to open the dryer doors, open the explosion venting windows and also to open the doors leading to a corridor. Burning material was distributed through the room and out into the corridor.

Eight sprinklers in the laboratory and two in the corridor opened and controlled the fire.

The number of sprinklers opened and evidence of charring of all wood surfaces indicates a fire of considerable intensity. It is evident that serious injury might have been expected if this had occurred while the laboratory was occupied.

CASE HISTORY NO. 881

Aluminized Composite Propellant Explodes During Mixing

Description: At approximately 11:40 p.m. on 1/2/63 a 100-gallon Read Horizontal mixer located at a solid propellant manufacturing plant exploded with a full charge (approximately 1300 pounds) of an aluminized composite propellant containing ammonium perchlorate. The incident occurred at the end of the first 20-minute vacuum cycle and immediately after the mixer blades were reversed. No personnel were injured. The building and all equipment included in the building were completely demolished. In addition 4 other structures suffered severe damage with minor damage observed in 12 other facilities. The incident was of short duration with no fires reported. The first mix was being made in the 100-gallon Read mixer following a monthly check by the maintenance department on 12/28/62. During this check the mixer bearing packing was changed in all the bearings, and the mixer was run for 50 minutes by the maintenance men. Also during this time a check was made for vacuum leaks and for bearings operating with excessive heat. Following the normal preventive maintenance check, the mixer was turned over to production with the recommendation that the mixer be operated further to break in the new packing. The mixer was operated empty for another 5 hours during which time vacuum and temperatures were observed to operate within the proper range. At the end of this check the mixer bowl was cleaned and prepared for the next mix. The mix progressed normally throughout the eight material addition steps, with the mixer being reversed for 30 seconds at the end of each of these additions. After blending the final addition of material, a 20-minute vacuum cycle was satisfactorily completed with the blades operating in the forward rotation. At this point in the mix cycle, as required by the mix procedure, the mixer blades were stopped for about one minute prior to initiating the reverse rotation cycle. As soon as the reverse button was pushed the mixer exploded. There were no personnel injuries although one operator was knocked to the ground when his helmet was struck by a fragment from the explosion. A detailed analysis of the blast area and fragments involved showed that a high-energy explosion occurred as opposed to a detonation. The confinement presented by the mixer bowl contributed significanty to the violence of the explosion. The damage sustained is comparable to that which would be expected from detonation of approximately 700 pounds of TNT. This represents approximately 25% of the total potential energy.

Cause: The cause of the explosion could not be definitely established from the blast pattern, analysis of fragments, or a review of the operating procedure used in the mix. However, because of the correlation of the time of the blast with the operation being performed, two probable causes were assigned.

1. A piece of tramp metal smaller than the 0.250-inch feed screen openings may have entered the mix and may have been nipped by the blade operating in the reverse direction.

2. A concentration of unblended perchlorate in the shaft seal housing could have reacted to the impact between the upper shaft housing and the shaft upon blade reversal and initiated a flame path to the mixer.

The appearance of pitting and flame scarfing on both a blade and on a mixer shaft allows either conclusion as to the source of the deflagration.

Preventive Measures:

1. All mix components are screened prior to adding to the mixer using screen meshes smaller than the mixer blade-to-bowl clearances.

2. All blade-to-bowl clearances have been increased to a minimum of 0.125-inch.

3. All mixers above 50-gallon capacity will be of the vertical shaft design as opposed to the horizontal shaft design involved in this incident. Thus, the possibility of deflagration initiating in the mixer shaft housings will be minimized.

4. The method of feeding the mixer has been revised so that the minimum number of perchlorate additions are made at the end

of mix cycle instead of the previous method of adding perchlorate throughout a large number of addition steps. By adoption of such a procedure the formation of the explosion sensitive matrix configuration is limited to a shorter period during the mix cycle.

5. Mixer blades are not operated in reverse direction during the course of a mix.

CASE HISTORY NO. 882

Polymer Plugged System-- Pressure Indicator Fails

Description: Just prior to the time of this incident, a separator was being tested for leaks by use of high pressure. The pressure had then been released using normal venting procedures and the pressure gauges on the test panel board indicated zero pressure. A pipefitter loosened the high pressure tubing connections and found no indication of residual pressure. As he bent over to complete the disconnection of the tubing, there was a mechanical failure of a fitting in the system. The stream of test oil struck his leg and knocked him down. The pressure continued to be released intermittently, forcing the man to crawl out of the area in order to avoid being struck by the swinging high pressure tubing. The pipefitter received a serious laceration of the leg, but was able to return to work the same day.

Cause: The plugging of the system with polymer from the test item was the direct cause of the incident. This polymer held pressure in the system in such a way that the gauges did not indicate that pressure existed.

Preventive Measures:

1. Piping system is to be revised to provide another pressure indicator and an additional method of venting.
2. The entire system has been completely inspected and cleaned, and in the future, items to be tested will be cleaned prior to testing.

CASE HISTORY NO. 883

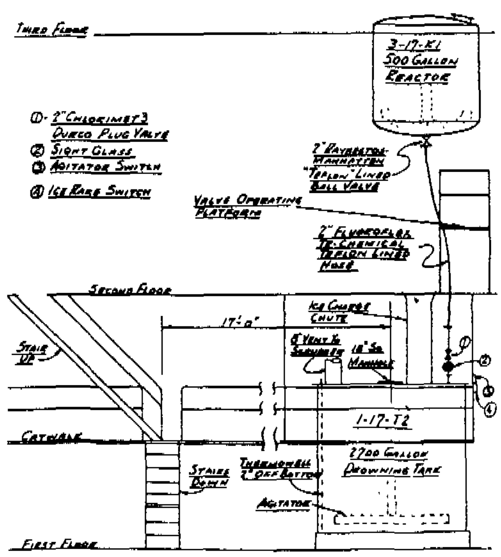
Exothermic Reaction-- Operator Fatally Injured

Description: An employee was discharging a batch of chemical intermediate from a five hundred gallon glass-lined reactor, located on a third floor level, through a two-inch Teflon-lined hose into a twenty-seven hundred gallon tank containing a mixture of ice and water, which was located on the first floor. (See diagram)

He opened the discharge valve on the reactor located on the second floor level, and walked downstairs to the drowning-tank location. Apparently, he must have noted a violent reaction taking place in the tank, because he closed a plug valve located in the hose, just above the tank. The temperature of the material in the drowning-tank rose rapidly and erupted out of the eighteen inch manhole, over which there was a loose hinged cover, burning the employee about the neck, face, arms and back and injuring him fatally.

Cause: Apparently the operator, after he had made up the ice and water slurry mixture, failed to check the plug valve above the tank to make sure it was closed or else, wrongly opened the plug valve before opening the discharge valve of the reactor. When he opened the discharge valve of the reactor, the full flow of the product discharged into the drowning-tank, overheated and erupted out through the tank manhole.

(The product is discharged from the glass-lined reactor, through a two-inch Teflon-lined hose to the drowning-tank. There was a two-inch Teflon discharge ball valve at the bottom of the reactor and a two-inch Durco plug valve, located just above the top of the drowning-tank. The operating procedure for the drowning operation is to first open and close the plug valve at the drowning tank to drain the hoseline, and then open the discharge valve at the reactor. Product feed flow is controlled by the operator through the plug valve above the top of the drowning-tank. Product flow into the drowning-tank is controlled so the temperature of the mixture is maintained at 5°C., which should take approximately forty-five minutes.)



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Preventive Measures: 1. This operation and similar types are presently being reviewed to assure product feeds are adequately controlled to prevent a similar type accident.

2. Operators have been re-instructed in the valving procedure for operations of this type to make sure they are following operating instructions.

3. A Job Safety Analysis program has been initiated in the department to make sure employees are complying with prescribed operating procedures, and operations are adequately safeguarded.

4. In addition, to facilitate operations, the control valve extension handle on the tank has been relocated near the temperature recorder and the exit side of the manhole. Also, the agitator switch and ice rake switch have been relocated to the exit side of the manhole.

CASE HISTORY NO. 884

Oxygen-Fed Fire Inside Air-Supplied Suit

Description: An employee received severe burns to the chest, shoulders, neck, stomach, and legs when oxygen-saturated cotton underwear ignited inside an air-supplied suit he was wearing.

After disconnecting the air supply and exhaust lines from his air-supplied suit and leaving the controlled atmosphere room, the employee removed his helmet and lit a cigarette. He then connected an air supply line from another room to his suit, to flush and cool the suit. This second supply had been provided for this purpose. Following these actions, the employee's underclothing caught fire.

Cause: Apparently, a spark from the cigarette ignited the oxygen-saturated cotton underwear which in turn ignited the suit. Two employees cut and tore the suit from the employee and beat out the fire, after which the injured employee was transported to the plant medical facilities for first aid treatment and then to the local hospital.

Investigation disclosed that the respiratory air supply to the second room, normally enriched by 2-3% oxygen, actually contained 68-76% oxygen resulting from the failure of the air-oxygen mixture control valve. This situation introduced a severe hazard to a procedure which otherwise had been determined safe and had been used routinely for some time.

Preventive Measures: Pending the installation of more reliable instrumentation and controls on the oxygen feed, addition of oxygen to the respiratory air system was suspended.

CASE HISTORY NO. 885

Sight Glass Booby Trap

Description: The operator had transferred material through a sight glass for a layer separation. After the separation, he closed the valves and went to the lunchroom to eat his lunch. While he was gone, steam from a leaking valve built up pressure in the sight glass (6 in. x 15 in. tube type). When he returned to make adjustments in the valves, the sight glass fractured. The ruptured sight glass showered broken glass in a 50-60 foot area. The employee received a severe cut on the right forearm and numerous small cuts about the face and head.

Cause: 1. A 150 lb. steam line was piped into a product line a week before the accident to dry and purge the product line after material transfer.

2. The valve in the vent line at the top of the sight glass had been shut, making the sight glass a part of a closed system that included the steam line.

3. Steam pressure built up in the sight glass because of a leaky valve.

4. Supervision and operators failed to recognize that 150 lb. steam pressure could be transmitted to the sight glass.

Preventive Measures: 1. The sight glass will be guarded by an ethocel enclosure.

2. The valve in the vent line has been removed to insure that the sight glass is always vented.

3. The steam line has been disconnected and a separate pump and transfer line will be installed.

4. A "Safety Audit" of all operations by supervision and operators will be performed to check for "booby traps" in equipment and procedures.

CASE HISTORY NO. 886

Static Charged Spray of Hot Toluene Ignites

Description: A fire occurred when toluene at 75^{o} was being recycled through a Sparkler type filter. The operator was at the

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filter manually bleeding off the air when he noticed the toluene surging in the line from the bottom of the vessel to the pump. He switched off the vessel agitator and the situation corrected itself quickly. Vapors then spurted out the filter-vent with such force as to cause a 4 to 5 foot, 1/2-inch polyethylene hose from the vent to flip out of a plastic bucket located on an adjacent table. Some seconds later a crackling noise was heard and the operator saw a flash of flames about his feet, and also at a wall behind the filter to his right. He ran for an extinguisher, heard further cracking noises and thinking an explosion was imminent he rushed outside. He and another man called the fire department and turned in the plant alarm. The fire was extinguished in 30 minutes, principally with foam.

Extensive damage resulted to service and chemical lines including electrical lines and instruments. The building was not sprinklered but structural damage was confined to windows and doors with superficial damage to reinforced concrete beams. A thick layer of soot was deposited everywhere, mostly from the 200 gallons of hot toluene in the extractor feeding the filter and consumed in the fire, when glass pipe lines broke from the intense heat.

Cause: Investigators believe that static ignition occurred when the hot toluene vapors issued from the plastic hose at sufficient velocity to blow the line from the bucket. Atmospheric conditions were dry. Prior to the incident a bad leak developed in the feed line to this extractor while 30 gallons of toluene were being pumped in. Toluene ran on to the floor and into the drain which was hosed down. A couple of hours previously, washes containing toluene were neutralized and released down the drain. The pump was checked and found in perfect working order. The bonding wires on the glass lines were intact.

Preventive Measures: Preventive measures will include installing a vent receiver, flexible bonded hose and sight glass, with the receiver venting outdoors through a flame arrestor.

CASE HISTORY NO. 887

Explosion Occurs During Vacuum Distillation of Methyl Azide

Description: A chemist was seriously injured when an explosion occurred while he was vacuum distilling methyl azide. He was either holding or shaking the trap containing the azide with his right hand when it detonated, seriously injuring his right hand. He also sustained superficial burns and lacerations about the face and chest. The shock wave broke the overhead fluorescent lights and bottles of organic reagents about the laboratory. Adjacent equipment in about 5 ft. wide area and vacuum lines were completely destroyed. Burning liquid and glass were spattered on the chemist and the right lens of his safety glasses was broken. Ordinary glasses in a pocket case were completely demolished.

Cause: The method of preparation used was the methylation of an aqueous sodium azide solution with dimethyl sulfate. Four previously successful preparations had been made in the same manner. The pH of this reaction is controlled at 5-7 by use of methyl red indicator and addition of sodium hydroxide if needed. If the pH was close to 5 or dropped for a short time below 5, then hydrazoic acid, a powerful explosive, can be formed and distilled out with the methyl azide. The investigators believe this may have occurred, and as in another case described in the literature, a slight shock caused mercury azide formed by reaction of the hydrazoic acid and mercury in the manometer to detonate.

This tragic accident is another example of the need for extreme care and taking every precaution when dealing with potentially hazardous materials.

CASE HISTORY NO. 888

Delayed Reaction from Stratified Sulfuric Acid

Description: On Monday, March 11, 1963, a new procedure for recovering acid ester was started. Prior to this time, no attempt was made to recover acid ester routinely due to severe fume problems. After a fume scrubber was installed, members of Production and the Technical Service Department experimented with recovery techniques and demonstrated the final procedure on Friday and Monday day shifts. The procedure was adopted on Monday for routine operations. Operating instructions were posted at the chief operator's desk and inserted as an addendum to the formal operating instructions at the operator's desk.

At the start of the split shift on Monday, the washer operator asked the chief operator to assist him in removing an alkaline wash. At about 5:50 p.m., they opened the valve in the alkaline wash line and began draining into an acidified heel in the acid ester tank located on the first floor. They then opened the sulfuric acid valve one turn.

Both the wash and the acid entered the acid ester tank through the same nozzle. The mixer was not running at this time nor at any time during the draining of the wash. The operating instructions specified that the agitator be left off because experience had shown that the bottom propeller was not submerged in the liquid until all the wash was in the acid ester tank and then only to a depth of one to five inches. The possibility of severe foaming with this situation was recognized and the operating instructions included a note to shut off the acid flow if this should occur.

The chief operator tested the wash and found it strongly alkaline. The wash continued to drain during this time. Three to five minutes later, the material foamed out of the manhole of the acid ester tank onto the floor. The chief operator told the operator to shut off the alkaline wash. He then went to observe the acid ester tank from the second floor and the ground floor. After noticing that the foaming was subsiding, he returned to the second floor to again drain the alkaline wash after a total elapsed time of two to four minutes.

After observing no further incident, the chief operator left for dinner at 6:05 p.m. About fifteen minutes later, when approximately fifty gallons of wash remained in the #6 washer, two operators heard a loud report and observed a geyser of material spraying from the acid ester tank manhole to the roof some twenty-six feet above the manhole of the tank. Both went to the east door and then returned to give aid. An operator who was operating in the south section went into the north section, then returned to call the guards and the dispensary.

Two operators were standing by the control panel on the third floor at the west end of the building. Their position placed them some fifteen feet above and in front of the acid ester tank manhole. The force of the eruption knocked them both down. In falling, they both lost their glasses and suffered lacerated knees. One began crawling because of the slippery grating and was found about fifteen feet away from the panel by another operator who immediately took him to the hose in the south section and washed out his eyes and flushed his body. He did not attempt to use the safety shower in the north section because of the material dripping from the underside of the roof. The injured also crawled to the safety shower on the third floor, stood up and turned it on. After remaining in the shower a short time, he went to look for the other operator, but when he could not find him, returned to the shower. Because of the fumes, he again left the shower and went into the south section. After finding the other operator who was being assisted, he returned to the north section and descended to the ground floor where he again showered with assistance. He was taken to the dispensary by the guards.

The following observations were made about thirty to forty minutes after the incident.

1. A 2 ft. by 6 ft. piece of floor grating above the manhole of the acid ester tank had been lifted out of place and turned sideways.
2. The acid valve was still open about 1/4 turn.
3. The liquid in the tank was still boiling violently. A check with congo red paper showed it to be slightly acidic.
4. A liquid puddle in front of the panel on the third floor tested faintly alkaline to brom thymol blue paper and slightly acid to congo red paper, indicating a pH of 5.0-6.0.

Cause: This accident was caused by stratification of concentrated sulfuric acid in the bottom of the tank as a result of inadequate mixing with subsequent sudden mixing and violent reaction liberating CO_2 and probably steam.

Exactly when the stratification occurred is problematical. Some accumulation could have occurred during this batch or even the preceding batch. However, the committee feels the major contribution to the buildup probably occurred during the period after the initial foaming when the acid line was left open while no wash was draining.

During this time, the acid stream was falling into a stagnant acidic aqueous solution, thus plummeting directly to the bottom with little mixing. A check of several batches showed a wash specific gravity of 1.05 to 1.11 versus 1.70 for 60° sulfuric acid.

The eruption apparently occurred after the alkaline wash reacted with the acid in the upper layer and had reached the lower layer of concentrated sulfuric acid. This type of reaction is known to occur suddenly and violently.

Preventive Measures:

1. Review and evaluate the acid ester recovery operations for possible benefits from a new or revised system. If the results of this study show that any continued use of the present system is desirable, the following changes should be made:
   a. Revise the mixer in the north tank to give thorough mixing under all conditions.
   b. Relocate the mixer starter switches and the main acid valve from their present positions above the acid ester tank manholes to a more remote location.
   c. Revise the acid piping so that the north and south tanks will be supplied by separate lines from the second floor with separate sight glasses and throttling valves.
   d. Provide a system for sampling the north tank from the second floor similar to the one in use on the south tank.
2. Completely review safety shower locations and number. Install at least one additional safety shower on the third floor.

3. Emphasize to all operators the need for use of the south tank agitator at all times during the acidification.

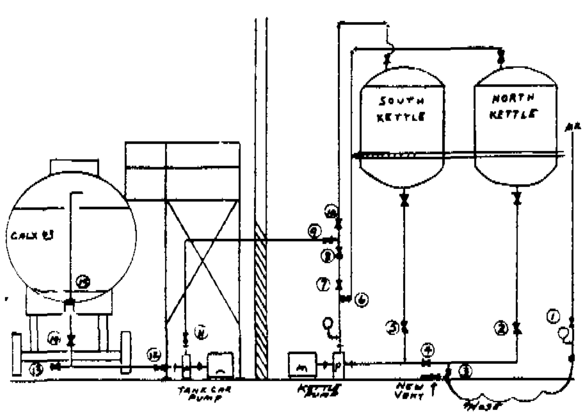
CASE HISTORY NO. 889

Sprayed with Chemical--Compressed Air Used to Clear Drain Line to Tank Car

Description: A railroad tank car, from which product is pumped into a process kettle several times daily, had been emptied except for a remaining six inch heel. Before disconnecting the car, the operator prepared to blow the transfer pipe line back to the tank car clear with air. (See sketch) He connected the air hose (at valve 3) to the transfer line, and applied air pressure (opened valves 1, 3, 4, 7, 8, 9, 11, 12, and 14). Noticing that mist was not coming out of the tank car dome, indicating air was not flowing back to the tank car, he shut the air off (at valves 1 and 3) and disconnected the air hose. He cracked a valve (at 13) open slightly and immediately closed it when product sprayed out. The employee went to the top of the tank car and attempted to move the foot valve (at 15) which was closed. The pressure remaining in the transfer line vented into the heel and splashed product out of the tank car dome onto the employee.

Cause: Employee failed to vent pressure remaining in the transfer line into the kettle (South Kettle--valve 10), before attempting to move the tank car foot valve.

(Note: The transfer line is blown clear with air through the tank car foot valve. When the operator, from a ground level location, notices mist coming out of the tank car dome, he shuts the air off, closes a valve (14) under the car, and closes the foot valve. After venting the remaining pressure in the transfer line into a process kettle (through valve 10), he disconnects the tank car.)



Preventive Measures:

1. Air-blowing pressure for clearing the transfer line will be reduced from 50 pounds to 15 pounds.
2. A new vent valve has been installed on the hose side of the air valve so the transfer line can be rechecked for pressure before the hose is disconnected.
3. Employees have been re-instructed to vent line pressure into the processing kettle before disconnecting the line or moving the tank car foot valve.
4. Employees have also been recautioned to place themselves in a protected location when checking blowing operations.

CASE HISTORY NO. 890

Autoclave Door-Locking Mechanism Failed

Description: Two employees were operating a large autoclave in a molding operation. The door (approximately 6 ft. in diameter) was blown open releasing steam and hot water into the room. One of the operators in the immediate area received minor and moderate burns to the arms and body.

Cause:

1. The autoclave door-locking mechanism had partially opened which allowed the door to blow out.
2. A short had occurred in the electrical system caused by accumulated condensate in the conduit resulting in intermittent operation.

Preventive Measures:

1. Seals will be provided to protect the conduit and switch boxes from condensate accumulation.
2. Install a mechanical lock device on the clamping ring which holds the door in the closed position.

CASE HISTORY NO. 891

A Construction Accident--Process Equipment Erection

Description: Two mechanics were injured when a heat exchanger fell and struck them. The exchanger weighed approximately 1200 pounds and was 16 inches in diameter and 17-1/2 feet long. One man suffered "multiple fractures of the 12th rib, fractures of the transverse process of the first four lumbar vertebrae and a fracture dislocation of the fifth vertebra." The second man was treated for "abrasion and severe contusion to the left forearm."

Three stainless steel heat exchangers were being installed. A one-ton chain fall was suspended from a short section of the "H" beam which was wedged, but not mechanically secured, between two floor beams above and near the location of installation. Using the chain fall, one of the exchangers was placed in position on two welded 5 in. x 28 in. brackets about five feet above the floor.

The heat exchanger has feet 5 inches long by 4 inches wide by 4 inches high located near each end. The one heat exchanger had been positioned with the two feet resting on the brackets but not bolted into position. Due to the weight of the exchanger there seemed to be no doubt that it would stay in position until the assembly was completed.

The second exchanger was brought under the chain fall on a four-wheel dolly. While one worker was adjusting the choker on the second exchanger, the first exchanger turned and fell off the bracket striking him a glancing blow across the lower back and pinning him between the two exchangers. He was severely injured. The other worker was struck a glancing blow on his left forearm. Seeing the first worker was pinned, the less severely injured man called to co-workers for help.

Cause: The cause of the heat exchanger's falling was at first thought to be due to either vibration or some externally applied force. In the reenactment of the accident, vibration was eliminated as a possible cause. It was found that two men could not apply sufficient force to turn the exchanger off its feet.

It was found that if the slack chain was allowed to fall over the top of the exchanger in place and foul either in the floor grating or around the four-dolly wheels, the slack chain would pull against one side of the exchanger when the operator moved the load chain down. The chain fall operator could do this with little effort. The force thus applied appeared to be the only force available that could have toppled the exchanger.

Preventive Measures: There are many lessons to be learned from this accident:

1. Always secure a load before detaching lifting device.
2. No one should ever work or stand under a suspended load or a load that is unsecured.
3. Be sure that equipment is handled and used safely, i.e., be sure that mechanical equipment, such as chokers, chains, chain falls, cables, etc., are not fouled or bearing on obstructions or equipment.
4. Secure the suspension of any chain falls, hoist, etc.
5. Evaluate all the hazards on a job and take the corrective action.
6. Proceed with caution.

CASE HISTORY NO. 892

Disconnected Hot Water Line Under Pressure

Description: An employee was disconnecting a hose from a line out of service and inadvertently disconnected a hot water line in service. When he disconnected the line, hot water gushed out causing first and second degree burns to his abdomen, arms and back.

Cause: Investigation revealed that there was nothing mechanically wrong with the equipment; however, the use of quick connecting couplings in high temperature service is poor practice and is to be discouraged.

Preventive Measures: Several points concerning this injury will be discussed in safety meetings throughout the plant as follows:

1. Check to see that pressure is off any line to be opened, and be sure that the correct line is opened.
2. Turn pressure gauge on pump so that it can be seen from the valve operating position.
3. Stand to one side when disconnecting hoses, or breaking flanges so as to be in the clear, if pressure should be on the line.
4. Do not use quick couplings in hot service, use Boss type fittings (available in Warehouse) equipped with a weep hole to provide warning of pressure on the line when the connection is loosened.

CASE HISTORY NO. 893

Explosion in Pump

Description: An employee was starting a direct coupled 1-1/2 inch stainless steel centrifugal pump. An explosion inside the pump caused it to rupture and pieces struck the employee's leg. He received a comminuted fracture of the right leg, including compound fractures above and below the knee and deep gashes and multiple contusions.

Cause: Investigation indicates that an explosion of organic vapors occurred inside the pump and/or connecting piping. The source of the explosion has not been definitely determined but it is possible that the impeller of the pump came in contact with some foreign metal.

Preventive Measures:

1. When the service of a centrifugal pump is to be changed, it must be flushed with water or nitrogen before being started. The same precautions are to be taken even though the pump remains in the same service if, in the opinion of the operator, there has been any possibility of the entrance of air into the system.

2. All operators are to be given verbal and written instructions concerning the correct way to start a centrifugal pump and the potential danger if a pump is run with valves in the discharge or feed line closed.

3. Signs are to be permanently attached to each centrifugal pump warning of the need to open the discharge valve before starting.

CASE HISTORY NO. 894

Started to Repair Acid Line Before Checking with Process Operator

Description: A piper was sent to the bisulfate department to make a repair on a line at the discharge of an acid pump. He was sprayed with muriatic acid from a flange which he had loosened in the course of this job. Prompt removal of his clothing, use of a safety shower immediately, and his wearing of goggles prevented any injury.

Subsequent investigation revealed that the following events led up to this near-miss:

1. The Pipe Shop foreman showed the job to the man one day prior to the incident.

2. The man proceeded with the job without checking with the operator of the department, per Pipe Shop rules. He then proceeded to loosen the flange, found it weeping, and then contacted the operator, who closed the inlet valve to the pump which is upstream from the flange and pipe on which he was working. The piper proceeded to break a union in the discharge line and at that point, was sprayed with the acid from the previously loosened flange.

Cause: The accident was caused by the piper's failure to observe Pipe Shop Department Safety Rules in doing this type of a job, including, particularly, the proper clearing of any lines on which he is to work and to coordinate this effort with the department operators and to wear full protective rubber gear in any such operation. Incidentally, he also failed to abide by the lock-out procedure on the pump in question, although this did not contribute to the accident.

Preventive Measures:

1. The piper involved has been disciplined for his failure to observe safety rules.

2. A supervisory safety meeting has been conducted to remind everyone of the responsibilities charged to them by the lock-out procedure.

3. All supervision has reminded all employees that adherence to safety rules and regulations is mandatory.

CASE HISTORY NO. 895

Hazard Recognized but not Rectified

Description: An operator in the pilot plant was sprayed in the face with a stream of polymer slurry. He suffered minor chemical burns to both eyes. Polymer in a hydrocarbon suspending agent is transferred from the reactor to a 500-gallon Pfaudler vessel. Alcohol is added to this vessel, and the mixture is heated, cooled and a sample taken for lab evaluation. Although the pilot plant had been in operation several weeks, this vessel had not been used but had been piped up. One week before this incident, the vessel was cleaned and during this cleaning operation, an operator discovered an open line on the pump discharge with a crows-foot connection on it. Rather than call in a pipefitter, the operator placed another crows foot with a downstream valve on the tank crows foot and completed the cleaning operation. In the rush, maintenance was never scheduled to complete the job properly. The injured operator opened the valve downstream of the crows foot to take a sample, and in the process the connection parted. Some of the slurry sprayed into the operator's face, causing the chemical burns.

Cause: Improper installation of piping and the subsequent parting of the crows foot connection.

Preventive Measures: Permanent piping was installed and the proper use of crows-foot connections was reviewed with both operators and supervisors.

CASE HISTORY NO. 896

Overcome by Fumes of Hydrogen Cyanide

Description: While working on a decontaminated HCN feed line to a reactor, an operator inadvertently opened a one-inch bleeder on the HCN feed line to an adjacent operating reactor. The resulting spill caused the operator to lose consciousness a short time later. He was breathing when help reached him and amyl nitrite was administered. He was taken to the hospital and released after one hour with no after effects from the cyanide; however, the fall resulted in two cracked front teeth.

During the same incident, after the bleeder valve had been closed by a supervisor, a pipefitter who assisted the supervisor and then stayed to wash down the spill was also overcome by HCN. After being administered artificial respiration and amyl nitrite, he, too, was sent to the hospital and released with no after effects.

Cause: The operator was overcome because of the combination of the following:

1. He opened the wrong valve without checking the valve line-up thoroughly.

2. He thought that the liquid was water and failed to recognize the exposure.

3. He was a relatively inexperienced operator and expected the cyanide to exhibit a more pronounced odor.

The pipefitter was overcome by taking too great a risk in the vicinity of the spill. Although familiar with HCN, he did not recognize that he was getting too much. He used a mouth mask part of the time, but it was not in place when he fell.

The design of the HCN feed system contributed to the incident since valves and lines to the various reactors were intermingled and confusing. However, both of the lines in this case were labeled within a foot of the bleeder lines and the "hot" bleeder was about three feet above the decontaminated bleeder.

CASE HISTORY NO. 897

Rain Shower Fractures Uninsulated Porcelain Pipe

Description: A sudden cold shower fell on an uninsulated section of porcelain line that contained hot vapors (120° - 130°C) from a reboiler to a column. The line cracked, releasing highly irritating vapors which traveled to a nearby building - people suffered minor eye or lung irritations.

Several lessons can be learned from this incident. All sections of the lines to and from the reboiler originally had been designated and installed as armored and insulated pyrex or porcelain. Operational difficulties required installation of a second reboiler. During the repiping job a section of previously armored porcelain was replaced with a different length of unarmored porcelain and the insulation was not replaced.

Cause: Porcelain, according to the manufacturer, should not be subjected to sudden temperature differences greater than 50°C (90°F). This occurred when the cold rain fell on the vapor line where the internal surface was at least 120°C. Armoring prevents or minimizes shattering but only the proper insulation can prevent a recurrence. Pyrex lines have a recommended maximum temperature difference of 160°C for 6 inch lines up to 200° for smaller sizes.

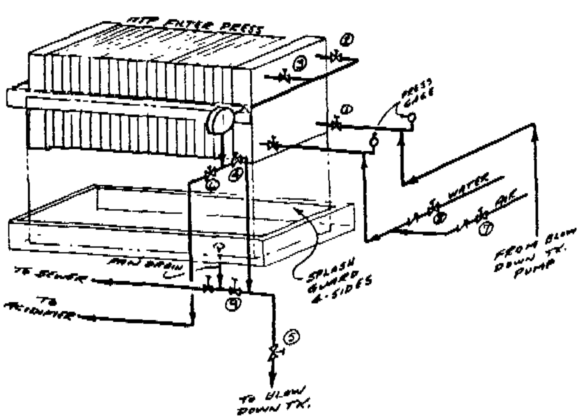
Preventive Measures: It should be made clear by the operating supervision that in any high hazard area where highly toxic, corrosive or irritating materials, or highly flammable or reactive compounds in mixture are handled, no changes in equipment, piping, pumps, valves and instrumentation, etc., are to be permitted without specific approval of the department head. Staff personnel are always available for consultation if the department head so desires.

CASE HISTORY NO. 898

Face and Eyes Sprayed with Alkaline Solution

Description: The employee had finished clarifying a batch of product solution through a filter press. He then washed the press with water returning the press rinse to the blow down tank and closed valve No. 1. (See diagram) He next opened the air valve No. 7 to blow the press dry, the filtrate going to the blow down tank.

The normal procedure after the press is blown dry is to close valves Nos. 2, 3, 4 and 7, and then open the press pan valve No. 9 to return the press drippings to the blow down tank. Before shutting off the air valve the employee closed valve No. 5 to the blow down tank which caused pressure to build up in the line. When employee



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opened the press pan valve No. 9 he was splashed in the eye and face with alkaline press drippings.

Cause: Employee closed a valve in a line used to drain the filter press pan while air was still blowing through the press which caused pressure to build up in the drain line. When the employee opened the valve, the pressure released through the line caused the material to splash.

Also, injury might have been minimized if employee had complied with instructions and worn his goggles.

Preventive Measures: Employees were re-instructed not to close a valve in the drain until the air was turned off at the press and the pan drained properly.

Employees were re-instructed to wear goggles when working with alkaline solutions.

CASE HISTORY NO. 899

Rescuers Not Prepared for Tank Entry

Description: When a contractor's employee was reported to have fallen into the wing tank of a barge, assistance was requested of the plant. The Plant Emergency Rescue Team responded. It appeared that the first man in the tank was being assisted by another contractor's employee. A member of the rescue squad entered the tank to render assistance but collapsed when he reached the bottom of the access ladder. Another member of the rescue squad entered the tank, and he too lost consciousness shortly after entering. The third member of the rescue squad donned a harness and a Scott Airpac and entered the tank with a life line and rescued the two plant employees and the two contractor's employees.

One of the plant employees was found submerged in water, and although a Pneolator and artificial respiration was used, he could not be revived. The other three men were revived. An examination of one of the contractor's employees revealed a fractured skull; the other two men suffered after effects of asphyxiation and shock. An analysis of the air in the tank showed a deficiency of oxygen (only 12%) and excessive carbon monoxide (6000 parts per million).

Preventive Measures: Safe Practices and Procedures for Entering Tanks and Vessels were in effect in the plant, but the importance of insuring that all personnel are instructed in the procedure and adherence to the principles contained therein, even in an emergency, will be emphasized to all employees.

CASE HISTORY NO. 900

Burned with Hot Caustic While Steaming Out Line

Description: Employee was assisting a mechanic to clean coating of carbonaceous material from the inside of a four inch pipe line. The pipe line which was approximately one hundred sixty feet high, had been disconnected from the top of a tower and was left open ended. About fifty gallons of a Caustic-Oakite solution was pumped into the line and the mechanic connected a steam hose to a valve fitting on the lower end to warm up the solution.

After the solution was warmed up, the line was to be filled with water to within about three to six feet from the open end. The injured employee climbed to the top of the tower to check the line. In the meantime, the mechanic slowly opened the steam line to warm the solution. Steam flowed through the line approximately two minutes. Suddenly the solution discharged with considerable force out the open end of the pipe. The employee who was standing on an adjacent platform was sprayed with the hot solution on the face and body, and his goggles were blown off.

Cause: The cleaning procedure was improper since the elevated open piping resulted in a spraying hazard and was not adequately safeguarded against boil over or splashes. (Probably the four inch line being cleaned had blocked with sludge during the steaming which caused a pressure build-up, and the solution blew out of the open end of the pipe when the block-up broke free.)

Preventive Measures: The present method of pipe line cleaning has been changed to eliminate the overhead boil over and splash hazard. The line will either be cleaned directly through the tower without breaking the line, or it will be piped to discharge into a safe location.

Present plant practices relating to handling of alkaline and acid solution are being reviewed, and new safety practices are being instituted.

CASE HISTORY NO. 901

Opening Vessels Under Pressure

Description: The employee opened a plugcock on a Chlorinator to gauge the contents (dip stick method). As he opened the plugcock, he was sprayed with a hot solution (80-85°C) of dichlorophenol. The injured employee received minor to moderate burns of the head, face, neck, arms and abdomen.

Cause: 1. The Chlorinator was under hydrostatic pressure due to over-loading. How this material was introduced has not been determined at this time, but it is believed that the fill line plugcock would have to have been open to introduce this much material.

2. The employee did not consider the possibility that the liquid level was higher than the inspection point and the vessel was under hydrostatic pressure. (The employee was following the written operating instructions.)

Preventive Measures: 1. Provide a means for safely assuring that the liquid level is below the inspection point before opening. This is to be done by providing a test bleeder valve.

2. Raise inspection valve to the floor level to avoid the necessity of using a ladder to reach the inspection point.

3. Stick measurements will be eliminated from these chlorinators.

4. "Supervision" are seeking the help of all employees to point out unsafe conditions and procedures in their areas so they can be corrected.

CASE HISTORY NO. 902

Pump Gasket Blew Out Spraying Caustic Solution

Description: An employee was assigned labor work near a caustic pumping system. An operator was in the process of putting the system in operation. The "heat up" steam line was frozen outside the building. The man doing the labor work near the pumps assisted the operator by passing a steam hose out the window and turning on the steam. The line thawed out and steam passed through the suction piping to the pump and up to the holding tank; this took about five minutes and is part of start-up procedures. The heat-up steam was then shut off.

The operator opened the 50% caustic storage outlet valve on the outside of the building and called to the other man to start the pump. After several minutes of pumping, the operator decided to have the other man shut off the steam hose and put it back inside the building.

As the man was closing the steam shut-off valve, he was positioned three to five feet from the pump and facing it. At that instant, the gasket between the pump suction plate and volute broke loose, moving out under pressure of the pump, creating an opening between the flanges and allowed caustic to spray out, striking the man on his face and neck. His injuries consisted of burns to ears, face, neck and cornea of the right eye.

Cause: The pumping of caustic from the storage tank to the pelletizing caustic head tank requires ten minutes each month. In extremely cold weather, the lagged caustic storage outlet valve and the pump located inside the building freeze. Procedure calls for steam to be introduced into the pump suction line at the outlet valve. This steam flows through the pump into the head tank and out its vent. Usually five minutes time is sufficient to heat this system, then steam is shut off.

Graphited asbestos gasket material is used throughout this system. It should be noted that there was no indication of gasket breakdown by leaking or weeping of caustic from the pump at the gasket joint between pump suction plate and volute. Possibilities for gasket failure are: (1) Shrinking and deterioration caused by alternated heating and cooling of the pump. (2) The possibility exists that the pump and gaskets could have been exposed to full steam line pressure of 140# psig if the pump discharge valve was closed during heat-up period or line blow out procedure at end of pumping.

Preventive Measures: 1. A light gauge metal cover has been installed over the gasketed joint that failed.

2. The present method of internally steam heating pipe and pump will be discontinued and another means will be provided.

CASE HISTORY NO. 903

Liquid Hydrogen Cyanide Sprayed on Head and Face

Description: While sampling HCN storage tank, the subject was sprayed on the face and head with HCN. He was immediately taken to the shower room, was stripped down and showered thoroughly. The plant nurse sent him to the hospital for observation and treatment. He complained of headache and nervousness.

The injured and a helper went to the HCN tank to get a daily sample as is normal practice. Earlier in the morning, two other men had been at the tank to get the sample but found the sample line and valve to be frozen so they deferred the job due to the extreme cold. It is normal procedure for any pair of qualified personnel from Building 46 to take samples, so the other two men went to the tank knowing the sample line had previously been plugged. Procedures followed were normal. The injured put on a gas mask and approached the sample line; his buddy stayed at the pump station with mask ready. The standby man turned the pump on as normal. Following sampling procedure, the injured throttled a 2 inch gate valve on the recirculating line returning to the HCN tank. This practice is necessary to obtain a slight pressure so that a sample can be drawn off. Slight pressure indication on a gauge above the 2 inch valve indicates when a sample can be drawn off. (See sketch)

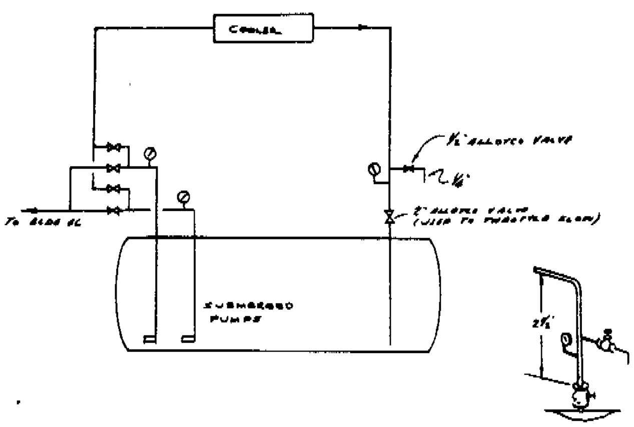
No pressure indication showed on the gauge. When he opened the sample valve, presuming pressure to be on the line, nothing drained into the sample bottle. He then opened the valve wider and suddenly the line cleared and HCN gushed into the bottle with force enough to splatter out on his face and head around his mask. He turned off the sample valve, ran to the emergency safety shower and found it was inoperative, presumably frozen up. His buddy put a Scott Air Pak on him so he would be breathing clean air free of the contamination from HCN on his body. He accompanied the injured to the shower room and dispensary.

When the incident happened, the two men were alone at the HCN tank. Building 46 was called by phone.

Cause: Extremely cold weather dropped the temperature just below the point where freezing of HCN could occur. The line must have been frozen right at the valve or just behind so that pressure on the full open valve was necessary to clear blockage. The result was a gush of liquid from the sample line.

Preventive Measures:

1. Install a shield and bottle holder, properly designed, on the sample line so that any splash or overflow will be deflected away from the operator. Build the shielded rack so the sample bottle will be inserted in a self-supporting rack or holder.
2. Install a pump switch at the sample station so the sampler can start or stop the circulating pump from the sample station. Include a pilot light on the switch to indicate pump operation.
3. Install a separate horn for the HCN tank farm alarm system so that in an emergency at the tank the building 46 operators can identify the emergency positively.
4. Install a set of flanges in the 1/2 inch discharge line from the sample valve. Fabricate and insert an 1/8 inch orifice between the flanges to restrict flow in case the valve is completely open. Insert the orifice so opening is in line with the bottom of the 1/2 inch pipe line.
5. Make certain the sample take-off line is horizontal. If needed, install a bracket to assure the line is held in level position to allow full drainage.
6. Remove old steel nitrogen purge line not now in use at the sample station.
7. Make it standard procedure in sub-zero winter weather to pour a bucket of hot water over the sample line to assure that the line is thawed.
8. Inspect and repair the safety shower and eyebath by the stairs to the HCN storage tank.
9. General Recommendation - That the plant safety committee study and establish procedures for the proper maintenance and use of emergency showers. That specific attention be given to check of showers before proceeding with hazardous material handling. Set a goal through plant improvement program to replace outside showers with others of standard design.



HCN STORAGE

CASE HISTORY NO. 904

Near Explosive Pressure Results from Decomposition of Overheated Batch

Description: In attempting to pump a batch of crude chloro (an intermediate) from wash vessel to a filter, it became apparent that the transfer line was blocked with a sulfurous mass. After failing to clear the blocked line with air pressure, the usual procedure of steaming the line was followed. The line was steamed intermittently for approximately six hours without clearing the blockage. During the course of the steaming, the temperature of the chloro batch in the wash vessel rose from 135°F to 210°F. Reasonable safe temperature for crude chloro at this stage is approximately 160°F. The temperature rise of the batch was not noticed.

After failing to unblock the transfer line with steam, the batch was pumped to an idle vessel. One hour later excessive pressure was built up in the idle vessel as indicated by a level gauge and by the rupturing of the gasket on the manhole cover of the vessel. At this point, the batch was intentionally discarded to the sewer to prevent a possible explosion.

Due to the hazardous conditions existing, operations were suspended for 2-1/2 hours and operations in adjacent buildings were suspended for one hour.

Cause: During the course of steaming the blocked transfer line, steam leaked up into the wash tank through its discharge valve which was not completely closed due to sulfur deposits in its seat. This steam heated the chloro batch in the wash tank to the point where it began to decompose. When the batch was transferred to the idle vessel it continued to decompose. Decomposition products blocked the flame arrestor cartridge in the idle vessel vent, and the ensuing pressure build-up ruptured the gasket in the manhole cover.

Preventive Measures:

1. Due to the instability of chloro at high temperatures, the importance of closely watching the temperature of chloro batches at all stages, especially during any steaming operations, was re-emphasized with all personnel connected with the chloro process. Under no circumstances will the temperature of the batch be allowed to rise above 160°F.

2. The use of air or steam to clear blockage will no longer be used. The pipes will be disconnected when a blockage occurs.

CASE HISTORY NO. 905

Condensate Return Tank Explosion

Description: On the morning of the accident, the work assignment was the first given to Mechanic "A" and Mechanic "B". The equipment concerned was a condensate return set, consisting of a cast iron receiving tank (28 in. x 28 in. x 16 in. high) and an external pump with float control. The tank had two crack leaks at the south retaining lugs (#6 and #7 on sketch).

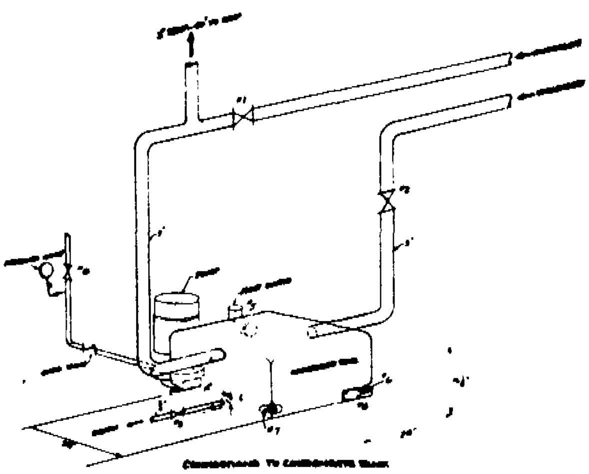
The tank was isolated by closing the two block valves on the two condensate supply lines (#1 and #2) and the pump discharge line valve (#8). The drain valve (#3) was opened and the inspection port plate (#4) removed to be sure all water was drained. This valving was all done by the Maintenance people, which is the standard operating procedure for working on condensate and steam lines at this location. The port plate was taken to the Maintenance shop for fabrication of a new gasket.

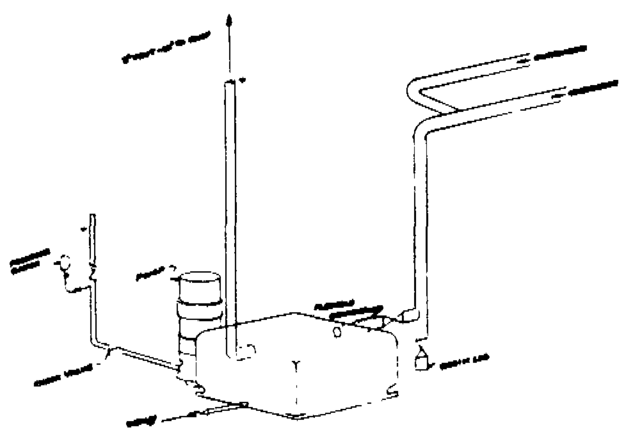
The normal vent to atmosphere for this tank was through an open 3 inch pipe in which there were no valves. (See sketch.)

When the tank was drained, the two cracks were ground (to a depth of a match) and the surrounding paint cleaned off. The welds were then made, using electric welding and nickel rod. The Maintenance Foreman was present at the scene when the welding was done by Mechanic "A". After completion of the welding, approximately 15-30 minutes (per Mechanic "B") elapsed to get the port plate and gasket from the shop, and install them on the tank. Another 5-10 minutes elapsed before the check of the repair started.

After closing the tank drain valve (#3), Mechanic "A" stood on the tank to reach valve (#1). Mechanic "B" was standing nearby (#7 on sketch) ready to hand Mechanic "A" a pair of channel locks, should he need them to adjust the packing gland on the valve. (This had been tightened when the valve was closed.)

As Mechanic "A" started to open valve (#1) the vessel ruptured with an explosive force. (Subsequent check disclosed the valve had been opened five turns. It took approximately twenty-two turns to open it fully. The valve is a standard 3 inch gate valve). Mechanic "B" was thrown back against some adjacent piping. Mechanic "A" was thrown into the air and over a sink stand, immediately south of the vessel, striking and breaking a wooden bench at the sink. He was found with his head, face up, against the sink with his feet resting on the bench. He sustained a





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depressed skull fracture at the forehead, a fracture of the right second metacarpal and abrasions of the elbows and thighs.

Conclusion: The accident was reconstructed, under controlled measures, as follows:

1. The vent line was removed from the tank at valve #1.
2. A one-inch line was installed at valve #1 leading to an empty 55-gallon drum.
3. All other valves were positioned as they were at the time of the accident.
4. A pressure gauge was installed upstream of valve #1 on the condensate line.
5. Two driers were started and valved into the condensate line. (Two driers were on the system at the time of the accident.)

After the above condition had existed for approximately the same length of time as on the date of the accident, the pressure in the condensate line was 126 psi. In three turns of valve #1, steam and condensate started to blow into the drum. When the valve was opened five turns, a flow of approximately 35 gallons of condensate was collected in the drum in a short period of time.

From the above, it is the opinion of the investigating group that, at the time of the accident when the valve (#1) was opened by Mechanic "A", the condensate trapped in the line was forced by the pressure in the line, past the vent and into the tank, compressing the trapped air in the tank, causing it to rupture with explosive force. (The 3 inch vent was opened the previous day as witnessed by one of the Maintenance Engineers.)

Preventive Measures:

1. In the future when condensate lines are to be worked on, and it is impossible to isolate equipment connected to the condensate line, condensate will be allowed to mix with cold water and then voided into a sewer.
2. Vent lines on condensate tanks have been and will be changed so that the vent will come directly off the tank to atmosphere, and will not be tied into any common header.
3. Drain valves will be installed upstream from the block valve, which will be next to the condensate tank.

CASE HISTORY NO. 906

Cumene Hydroperoxide Explosion

Note: The following is a translation of a letter received from West Germany where the incident occurred.

"We carry out the manufacture of phenol and acetone, using the cumene process. The cumene is oxidized with pure oxygen to cumene hydroperoxide. The resulting oxidate contains about 15% cumene hydroperoxide. Following this, the substance is evaporated under vacuum in a concentration plant. This proceeding is accomplished in three stages, after which a product results which is 50 to 60% cumene hydroperoxide.

"This product is broken up with a weakened sulfuric acid catalyst, from which the principal results are phenol and acetone. Through further neutralization in a distillation apparatus, these products are worked up to pure phenol and pure acetone.

"The explosion occurred in the second stage of the concentration process, from which a product results which is 30 to 35% cumene hydroperoxide.

"The working temperature in the concentration apparatus runs between 100^{o} and 110°C. On the day of the explosion, the whole apparatus was being operated at 109°C. At the time of the explosion, the second stage of the operation was not in operation. The receiving vessel, which was of a volume of 10 m^3, contained about 6 - 7 m^3 of 36% intermediate product. The container was blanketed with nitrogen. In addition, it was provided with temperature measuring equipment. The indicators of the temperature instrument were in the measurement station. The instrument for controlling and making safe the working temperature of the process was both visual and acoustical. These instruments are currently being revised.

"The explosion occurred five hours after the second stage of the concentration apparatus was taken out of operation - that is, when the around 35% cumene hydroperoxide had been stored for the stated period at 109°C. According to operating personnel, nothing unusual occurred or was noticed in the temperature gauge. Immediately before the explosion, white steam was seen at one place in the container.

"The reason for the explosion is still unclear. Possibly it was of catalytic origin."

CASE HISTORY NO. 907

Mixed Chloronitrotoluenes Explode

Description: An 8 ft x 20 ft. horizontal tank reboiler containing mixed chloronitrotoluenes exploded, causing extensive damage to adjacent equipment and the adjacent four-story brick and metal-sided building containing other equipment. Fortunately no one was seriously injured.

An exothermic reaction was started which first opened the 10 inch pressure relief vent, but within about 30 seconds generated sufficient pressure to rupture the vessel, which was designed for a 50 psi working pressure.

The operator, who was on the top floor of the adjacent building, heard the pressure relief blow and left the building by an outside stairway. He was about 150 feet from the building when the explosion occurred.

The tank was ripped open and flattened. In addition to smaller missiles, a few pieces of pipe and other metal weighing up to several hundred pounds were thrown from 300 to 800 feet. A number of plant buildings within a radius of 500 feet suffered broken windows and minor damage. A fire in the adjacent building resulted from the spray of flaming unreacted material from the ruptured tank. The automatic sprinkler system inside the building, though damaged, held the fire in check until it was extinguished by plant fire fighting personnel.

Cause: The explosion was apparently caused by the addition of caustic soda solution with the chloronitrotoluene feed to the still. The feed stream had been inadvertently contaminated with the caustic in a tank car used for storage purposes. Upon addition to the still, which was indirectly heated by an attached heat exchanger, an exothermic reaction was started which rapidly developed into a runaway pressure buildup.

Preventive Measures: Plant procedures for loading, labeling and sealing tank cars for intra-plant service will be studied and revised as found necessary.

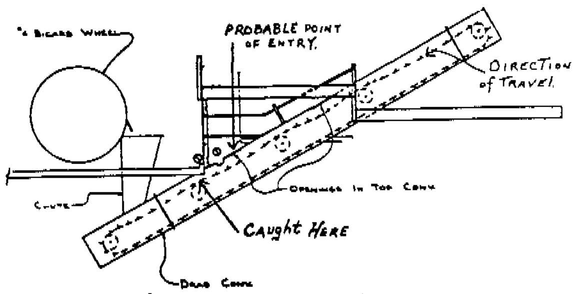
CASE HISTORY NO. 908

Conveyor Fatality

Description: The Process Wheel Operator in a bicarbonate of soda plant was found downward in a drag chain paddle conveyor, where he had been carried by the top run of the chain until he was wedged between the top of the conveyor and the chain. It was necessary to cut away sections of the conveyor with a cutting torch in order to free the victim. He was fatally injured. There were no witnesses to the incident which involved the victim's entry into the conveyor.

Cause: The conveyor opening involved in this incident was at the rear of the hopper and platform. The platform was protected by standard approved handrails with the intermediate hand rail located midway from floor level to top of railing. The conveyor was covered with hinged metal covers with the exception of two openings used for observation of operation of chain carrying the product away. The hopper plugged with bicarb and the victim asked if it could be unplugged from below by rodding down in the conveyor the opening above the hopper, but he was told this was impossible. The next time the co-worker's attention was brought to the activity of the victim, he was observed in the conveyor being dragged through the lower open end. He was forced to leave his normal operating area and place himself outside the walk-way and handrails in order to get into a position on top of the conveyor where it is thought he went into the conveyor. It has been concluded there was human failure and violation of safe operating procedures.

Preventive Measures: Although this operating equipment met the requirement of the State Safety Code, there was an opening in the conveyor outside the working area. Grid covers will be provided where inspection ports are necessary. Operating instructions will be issued prohibiting employees from passing over railings when equipment is in operation. More strict enforcement of safety rules to be applied, specifically the lock-out procedure when equipment is in motion.



CASE HISTORY NO. 909

Alkyd Resin Overflows Kettle

Description: Two drums of rework material were to be added to a thin batch of Alkyd resin (about 320°F) in a kettle. Because of incompatibility with other resins in the system, this resin was to be added directly to the kettle rather than pumped into a thinning tank as is normally done. The first drum was added without incident and the second drum had been placed in a horizontal position on a fork lift truck over the open manhole (about two feet above flow level). When the two-inch bung was removed and materials started to flow into the kettle, the two operators and foreman present noticed that the material was unusually viscous and that there was also a thin liquid flowing from the drum. Because this liquid had no odor, they suspected the presence of water. However, before the addition could be halted, the resin in the kettle overflowed, splashing on the two operators, one of whom slipped and fell in the spill. Both sustained burns to multiple parts of the body. Fortunately, their safety glasses protected their eyes.

Cause: The drum had been stored upright outside and water apparently had seeped into the bung gasket over a period of months.

CASE HISTORY NO. 910

Increased Hazards During Training

Description: The injured employee was instructing a new man for the first time to prepare samples of synthetic rubbers to determine their viscosity. He instructed the new coworker to open a nitrogen needle valve on a compressed gas cylinder. Excessive nitrogen pressure blew the plastic tubing (from the sulfuric acid scrubber) off the glass connection to the sample bottle. The sample bottle was being heated in a hot oil bath (135°C). Cold concentrated sulfuric acid (5-10 ml.) and hot oil sprayed out onto the man's face, neck, abdomen, and hands burning him.

Cause:

1. An inadequate pressure regulator was used. (The type used is the standard valve used for small cylinders.)
2. Opening of the needle valve permitted the direct flow of nitrogen from the cylinder to the sulfuric acid scrubber. A smaller Hoke valve located in this line had not been closed.
3. A shield was not provided for the bath and scrubber apparatus.

Preventive Measures:

1. Proper regulating valves and pressure reducing devices will be used to insure delivery of safe amounts of gas.
2. Shields will be provided to protect against splashing corrosive chemicals and equipment rupture.
3. Where corrosives are used for drying gases, other means will be considered to obtain dry gas wherever possible.
4. Laboratory supervision will increase their observation and instruction time during the "period of increased hazard" while a new man is being trained.

CASE HISTORY NO. 911

Acetaldehyde Vapor Ignited

Description: Suction to an acetaldehyde feed tank had been lost. To regain suction, it was necessary to bleed off the pump through the sample draw-off. A hose was attached to the draw-off and extended to a point outside the pumphouse.

Acetaldehyde vapors traveled approximately twelve feet and were ignited spontaneously by the heat from a steam line in the pipeway.

Preventive Measures: All personnel at this unit are instructed to bleed this pump into a flume well removed from any source of ignition.

CASE HISTORY NO. 912

Tried to Tighten Plug Before Pressure was Released

Description: A 1-1/2 inch steel pipe plug blew out of a screwed fitting just as a mechanic commenced to tighten it to stop a leak.

The work was on the new third stage surge bottle of the recently supercharged synthesis gas compressor. Because of thread leaks, the previous shift crew had reworked all of several plugs used on the bottles. At the time of the incident the compressor was operating on nitrogen gas with 1200 psi pressure. The decision to tighten the leaking plug while under pressure was made without realizing that plug thread engagement had created a precarious situation. Actually the plug was hand tight and engaged only one or two threads. Special detailed instructions by mechanics' supervisor probably prevented injury to the man.

Cause:

1. An incomplete job was not recognized.
2. The work was attempted while still under pressure.

Preventive Measures:

1. No attempt will be made to tighten fittings under pressure.
2. All foremen and mechanics will be reinstructed concerning adequate thread engagement on piping.

CASE HISTORY NO. 913

Use of Glass Annealing Oven As a "Burn-Out" Oven

Description: A 2 ft. x 2 ft. x 4 ft. (inside dimensions) electrically heated, circulated air oven designed for annealing glassware was also being used to "burn-out" partially polymerized residues from Pyrex glass tubes. The oven was located in the Glassblowing Shop.

At 8:15 p.m. the glassblower completed a charge to the cold anealing oven of glassware for annealing and of about one hundred 16 mm. dia. x 150 mm Pyrex tubes which contained partially polymerized residues. The oven was started on its automatic temperature-time cycle and the glassblower immediately left for the day. Approximately 5 minutes later the night chemist, on entering this laboratory wing on routine duties, heard an explosion. Investigation of this area by the night chemist showed that the explosion had occurred inside the glassblower's annealing oven. No fire ensued. No one was injured as there was no one in the Glassblowing Shop at the time of the explosion. Soot from the hydrocarbon combustion, as well as glass fragments from glassware which had been stored on top of the oven and broken and scattered by the resultant force of the explosion, covered all horizontal surfaces. The black soot also covered all other exposed surfaces in the Glassblowing Shop. The seams at the mid-section of the electric oven were forced apart by the explosion. Almost all of the glassware inside the electric oven was left intact. It was estimated by time lapse that the explosion occurred when the oven temperature indicator was showing about 200°F.

Cause: Monomer vapors had distilled from the glass tubes in sufficient quantity to form an explosive air-monomer mixture within the confines of the oven. The circulating air fan within the oven carried the air-monomer mixture to the area which housed the heating elements. The heating elements were at or above the auto-ignition temperature of this combustible mixture. Since the fuel, oxygen, and ignition source were simultaneously present, the explosion occurred.

Preventive Measures:

1. An oven which is designed for "burning-out" polymer residue from glassware is being considered. Until this type of unit is available, all Pyrex tubes containing polymer residues will be discarded.
2. Nothing other than clean, solvent free glassware will be placed in the electric annealing oven. Any other item to be heated in this oven must first be cleared with the Laboratory Section Manager and the Safety Engineer.
3. All equipment in the Research Centers will be checked for unauthorized use.

CASE HISTORY NO. 914

Non-ASME Vessel Ruptures During Test

Description: An air conditioning mechanic was testing an improvised pressure vessel for leaks when the vessel suddenly ruptured and seriously injured the mechanic.

This particular vessel has been used, over a period of from 5 to 10 years, to charge the mill roll storage air conditioner with oil. This air conditioner must be oil charged about twice each year and is the only unit in the plant that is so charged.

The injured mechanic recently improvised a leakproof top for the vessel from a 150 lb. forged steel pipe flange, wing nuts, bolts, rubber gaskets and sealed pipe fittings. Previous to the accident he had made new gaskets and resealed all piping joints. After the seals were dry he tightened the improvised top to the vessel and introduced "freon" gas, from a partially used 41 pound cylinder, to the vessel.

While charging the vessel with "freon" he probably was preparing a snifter torch to test for leaks and while so preparing, near the charged vessel, the vessel ruptured and the upper part of it struck the mechanic in the face. He received a comminuted fracture of the skull.

Cause: The vessel is made from three parts of sheet steel. The shell, which is 20 G. material was held to a slightly thicker bottom by lead solder. The entire interior was tin-lined. Neither the vessel nor the improvised top are of approved type. No regulator with gauge was used by the injured mechanic to control pressure being introduced to the vessel, or contained in the vessel. No shield or barricade was used while the test for leaks was being made. No pressure relief valve or blow-out plug was installed on the improvised top. Heat was no factor as the testing torch was evidently not lighted.

Preventive Measures:

1. Inspect and review all plant vessels on gaseous service that are not stamped approved, in accord with ASME code. Piping connected to these vessels should be included in inspection.
2. Discard and replace unapproved pressurized equipment.
3. Anchor pressurized portable cylinders regardless of size or capacity.
4. In pressure testing any equipment use hydraulic means where possible. If this is not possible use a secure baffle to prevent injury.
5. Use only pressurized vessels that are constructed in accordance with the ASME code and never exceed the prescribed working pressures.

CASE HISTORY NO. 915

Improperly Used 55 Gallon Drum Blew Up

Description: A 55 gallon drum blew up when the drum was improperly used as a product receiver on an experimental unit operating at 1500 pounds pressure. Fortunately, no one was injured.

Cause: The drum was overpressured while the unit was being brought on-stream. Operating personnel were placing the liquid level controller on the high pressure (1500#) separator in service and failed to close a bypass valve near the level controller. When the block valve downstream of the controller was opened, the entire system was dumped into the drum. Because the drum was designed for venting only the normal release from the separator, the pressure surge bulged the bottom, blew out the top and sprayed the contents over a wide area. No flash occurred even though a quantity of pressurized hydrogen was also released.

Preventive Measures: The overpressuring of any vessel creates severe injury possibilities. This incident was reviewed with the Engineering-Design Group who will see that equipment is designed and located to permit safe operations under both routine and emergency conditions. Also, all new or significantly modified units will be inspected by the Unit Safety Inspection Committee.

CASE HISTORY NO. 916

Implosion of Ammonia Tank

Description: A 40,000 gallon horizontal tank used in aqua ammonia service was emptied. Personnel then started the flow of water preparatory to making up a new batch. The water flows through overhead sprinklers inside the tank and the anhydrous ammonia flows via bottom pipes in the tank. Immediately after the flow of water began, the tank imploded, collapsing to perhaps half of its original volume. The tank was a total loss. Windows in the building were broken from the inrush of air. There were no personnel injuries.

Cause: Emptying the tank of its aqua ammonia left ammonia vapors in the tank. The tank was provided with a one inch vent which was open and a two inch vent which was closed. Turning water into the tank immediately scavenged all the ammonia vapor, creating a nearly complete vacuum, thus permitting the tank to collapse from atmospheric pressure.

Preventive Measures:

1. A sizeable heel of aqua ammonia should be left in the tank at all times except when the tank is being cleaned.
2. The make-up water should be supplied not through the overhead spray type arrangement but via a bottom inlet.
3. Whenever it is necessary to empty the tank completely, top and bottom manholes should be opened before adding any water to the empty tank.

CASE HISTORY NO. 917

Unsafe Acid-Treating Procedure

Description: Employee was etching stainless steel pipes with nitric acid prior to welding or soldering. He stood several lengths of pipe on end in a five gallon open bucket containing nitric acid, and leaned the other ends against a fifty-five gallon drum. One of the pipes slid off the drum, causing the other pipes to fall, and the pail containing the nitric acid tipped over. The acid spilled against a pallet that was nearby and splashed the employee about the head and shoulders. Employee was not wearing eye protection or any other personal protective equipment. (See sketch)

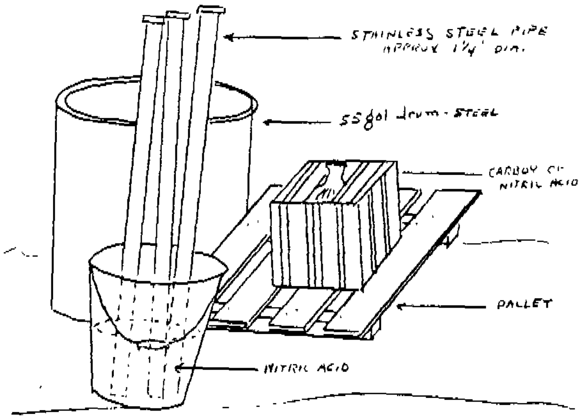
Cause: Unsafe acid treating procedure by employee who failed to make sure the bucket was secure and top adequately covered against possible splash.

Also, if employee had worn proper protective apparel, including eye-protection while working with acid, injuries might have been minimized.

Preventive Measures: Acid etching procedure has been changed so that dipping will take place when required in closed containers, in secure locations.

An eye-protection program has been established in accordance with Safety Standard for Methods and Equipment S-8, "Eye Protection," and reviewed with all concerned personnel.

Employees, working with corrosive material, have been instructed to wear proper protective apparel.



CASE HISTORY NO. 918

"T" Fails in Acid Line

Serious burns of the back, face and arms resulted when a mechanic was sprayed with 110°C, dilute (17%) HCl. The injured was working off a

6 ft. ladder painting flanges on a 2 inch pyrex line containing the hot solution. He claims that he noticed a sudden vapor leak at one flange of a "tee" in the piping system, and instinctively turned away from the vapor when the "tee" broke drenching him with the hot liquid. He tore off his shirt and goggles while running to and getting under an adjacent shower. He suffered extensive first and second degree burns and possibly some third degree burns, and required hospitalization.

There is no explanation for the sudden failure of the pyrex "tee" at all three joints. The injured claims he did not fall or lean against the vertical run of the pipe containing the "tee". The piping had been insulated originally but the insulation was removed and never replaced. Recommendations had been made to reinstall the insulation which would certainly have minimized the spray. The piping will be field armored as soon as possible. This incident points up the value of armored piping where dangerous materials are being transferred.

CASE HISTORY NO. 919

Inhalation of Chlorine Gas

Description: A considerable amount of chlorine gas was generated and released in a work area by the overflow from a process filter and HCL acid entering a sewer at the same time. An operator wearing a small inadequate mask, inhaled a considerable amount of gas before he made a switch to a larger cannister mask. He received first aid treatment and finished the shift. The following day he experienced some difficulty with his breathing and was advised to stay off work by his doctor.

Preventive Measures:

1. In the future, caustic will be added from the neutralizing tank during acid washing procedure.
2. Discharge lines from the filtrate receiver and the filter will be separated so that each tank is pumped separately to the decomposition area.

CASE HISTORY NO. 920

Acetic Acid-Caustic Potash Mixture

Description: An employee was pouring Acetic Acid into a Catalyst Pot, which had previously been used for addition of KOH. Residual KOH reacted with the Acetic Acid, causing chemical to blow back through fill line and spray onto the employee's face, head and shoulders. Investigation revealed that the employee was wearing eye protection but not the type prescribed for this operation. He received chemical burns to both eyes, face and shoulders.

Preventive Measures:

1. A separate location will be used for the addition of Acetic Acid (treatment tank) to prevent mixing of KOH with Acetic Acid.
2. Safety rules pertaining to the handling of chemicals will be strictly enforced.

CASE HISTORY NO. 921

Manhole Plate

Description: A pipefitter and his helper were removing a manhole plate from a blow tank. They had removed all the bolts except one which they intended to leave in place so that the plate could swing clear of the opening. The plate did not swing clear as they had anticipated and a small opening around the plate allowed the liquor to spray out striking the two men, burning them on the legs and arms. Investigation revealed that the liquor in the tank was above the manhole plate and gravity caused the liquor to spray out of the crack around the plate.

Preventive Measures: A gate valve will be installed at the bottom of the blow tanks so that the liquor can be drained before the plate is removed.

CASE HISTORY NO. 922

Boiler Inspection

Description: Mechanic was working on top of an exit gas duct from a boiler assisted by another mechanic, who was standing on an adjacent platform. Both employees were preparing the boiler for an annual inspection which was to be made on the following day. The mechanic opened an inspection port on the waste heat boiler and hot water was immediately released spraying him about the body. As he slid from his position on the boiler to the ground, he continued to be in the stream of escaping hot water.

Cause: Failure of the supervisor, who issued the safety work permit, to make sure the boiler was empty before issuing the permit. (The waste heat boiler had been taken out of service that morning after having been cooled for some time and the mechanics were instructed to drain the boiler and open the manhole to prepare for an annual inspection. A single safety work permit was issued by the supervisor to break a flange on the boiler blow-down system which is the only way the boiler can be drained and also to open the inspection port. The two jobs covered on the permit were begun simultaneously.)

Preventive Measures: This accident was reviewed with all supervisory personnel at the accident site and plant safety procedures involved in the opening of process vessels for inspection or entry were reviewed with all supervisory personnel.

The hazards of relying on gauges or instruments as the sole means of determining internal condition of process equipment was reviewed and supervisors were cautioned to make sure that equipment was emptied before safety work permits were issued.

CASE HISTORY NO. 923

Hoist Chain Failure

Description: Operator was attempting to remove the lid from a special reactor by means of a one-half ton hoist which was attached to the drive mechanism which is an integral part of the lid. The employee could not get the lid to release from the vessel and requested the aid of another operator working in the area. The other operator positioned his hand above the operator's hands on the hoist chain. As both operators were pulling on one chain, a link on the load chain snapped suddenly and the second employee's elbow swung around and struck the injured employee on the nose.

Cause: The load chain failed when excessive force was exerted by both operators on the hoisting chain possibly because the hoist capacity was insufficient to lift the lid drive unit from the viscous mass of the reactor or the load chain was kinked.

Preventive Measures:

1. The half-ton chain hoist has been replaced with a one-ton capacity hoist.
2. The lid lifting operation has been restricted to a one man operation and the operator has been instructed to report any hoisting difficulty to the supervisor.
3. The hoisting apparatus has been redesigned to provide:
   a) A permanent clevis arrangement to provide a more stable method for hooking the hoist on to the lid drive mechanism which will insure a straight pull on the load chain and eliminate the possibility of kinking.
   b) Lifting lugs will be installed on the lid to permit the lid to be lifted separately should the reaction mass stick to the agitator.

CASE HISTORY NO. 924

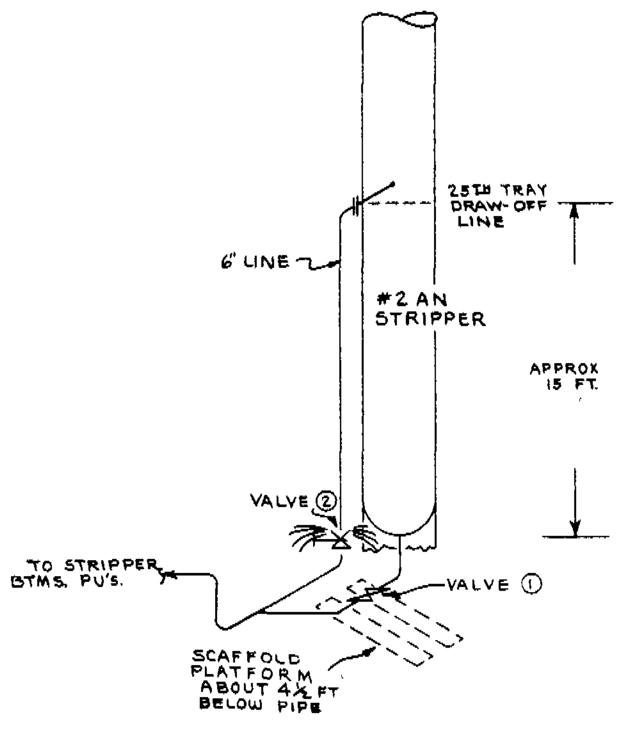
Stripper Column Maintenance

Description: Mechanics were preparing a chemical stripper column for maintenance. The column had been steamed, washed, vented, and isolated at all process lines. They removed one valve (valve No. 1, refer to sketch) and drained the trapped water from the low point in the pipe. After the mechanics had removed valve No. 1, they opened valve No. 2 to allow liquid in the draw-off line to drain out through the opening. A trickle of liquid came out. The mechanics then removed all of the flange bolts holding the valve, except two which were loosened. The flange separated slightly and there was still no sign of liquid. One mechanic then removed his goggles and started to remove the remaining two flange bolts. As he did so, water and sludge sprayed from the spread flanges of valve No. 2, striking the employee in the face and eyes.

Cause: The valve in the six inch draw-off line is used infrequently (during start-ups for example) and the line was plugged just above the valve.

The employee presumed the line was clear and removed his goggles before completely opening the line flanges.

Preventive Measures: Procedures have been established to make sure pipe lines are checked for plugs or obstructions prior to opening.



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This accident was reviewed with all plant personnel and the importance of not removing personal protective equipment, such as goggles, until pipe lines are completely cleared, was stressed.

CASE HISTORY NO. 925

Common Feed Lines

Description: During the feed of mixed acid to a nitrator, an explosion occurred in the acid feed line. The force of the explosion shattered a rotameter tube, blew out a flange gasket, bulged a blanking disc in the feed line and caused glass to be blown into the face, eyes and body of the operator. The operator received superficial cuts on his face and body. Glass particles were successfully removed from his eyes, with no permanent injury. The glass did not originate from the rotameter tube since it was enclosed in a pressure casement. The glass is believed to have originated from a broken light bulb. The operator was not sprayed with acid.

This nitration was the third batch of a series. The feed had been in progress for one hour and 50 minutes prior to the explosion. Prior to this series of batches, the feed system had been used to feed an organic liquid to another product reaction.

Cause: Investigation produced only a probable cause of the explosion. It is believed that the violent reaction resulted from contact with organic material retained in the asbestos flange gaskets, rotameter packing or in a dead-end section of the piping.

Preventive Measures:

1. This area will be designated a goggle area during all operations.

2. All flange gaskets, valve packing and rotameter packing will be changed from asbestos to Teflon.

3. Piping has been modified to eliminate all "dead-end" sections as well as some common use.

4. When changing from one product to another, clean-out procedure shall include dismantlement of acid feed piping to insure cleanliness.

CASE HISTORY NO. 926

Inadequate Respiratory Protection

Description: After a digester had been blown, strong SO_2 gas and steam blew out through the top, forcing the workmen to leave the floor and go out onto the roof. A side relief valve had been left in the "open" position, permitting steam and gas from an adjacent digester to feed back through the common header into the subject digester.

After the men had evacuated to the roof, a Digester Helper went back to make sure all personnel were clear. He put on a full face mask. The mask was not properly fitted and gas leaked into it. When he got back to the roof, gas had accumulated there. He was in a heavy concentration when he removed his mask.

The Fire Patrolman was servicing gas masks in the building. As he stepped off the elevator onto the floor he noticed strong gas and steam. Putting on a full face "all purpose" mask, he walked along to make certain all personnel were clear. The steam was very dense and he had difficulty finding the door to the roof. Gas came through the mask. He was exposed in a heavy concentration for three to five minutes. (Only the Fire Patrolman's exposure resulted in lost time.)

Cause: In neither case was the respiratory equipment adequate. A Chemox or Scott Air Pak is available for such emergencies.

Preventive Measures: Monthly instruction is scheduled for each person on proper use of respiratory equipment.

All personnel have been advised that area emergencies are taken care of by operating personnel in charge of the equipment. All others are to get out and stay clear unless asked to help. In such cases, adequate protective equipment must be worn.

CASE HISTORY NO. 927

Improper Hook-Up for Loading Caustic Tank Car

Description: An employee was loading a tank car with 50% caustic. There was a surge on the filling line as the pump was started, causing the filling line to come out of the tank car dome opening. Caustic under pressure sprayed in every direction, striking the employee in the face and on the body. He received alkali burns in the mouth, eyes, on both ankles and on the left leg.

Investigation revealed the following:

1. A center loading car was positioned under the loading station used for offset cars only.

2. The car was poorly positioned causing hose cramp in filling line.

3. The tie chain used for fastening the filling line in position was improperly attached to car.

Preventive Measures: Immediate action was taken to replace the flexible hose with a section of steel reinforced hard suction hose. Review operating instructions with all operators and provide positive position for loading line. Engineering to redesign loading station in such a manner as to eliminate problem of off-center and center loading car.

CASE HISTORY NO. 928

Pressure Vessel Reactors

Description: An employee was preparing to transfer a reaction vessel (12 in. x 2-1/2 in.) from a low temperature bath in a bench hood to a pressure reaction cubicle. A halogenated olefin had been introduced into the vessel and then nitrosyl fluoride was added. The temperature of the vessel was about -78°C. After a short time, when no pressure was observed, the employee started to remove the vessel from the bath and it ruptured. The employee received severe injuries to the lower abdomen and injuries to the hands.

Cause:

1. Using too large a sample of reactants which detonated, rupturing the reaction vessel.
2. The vessel was of an alloy that had less impact strength at low temperatures.
3. The loaded reaction vessel required transferring from the hood to a cubicle.

Preventive Measures:

1. Experiments of this type will be loaded, reacted and vented using proper shielding and remote handling techniques to prevent exposure to any employee.
2. Supervision will make certain that the quantity of materials shall always be kept to the absolute minimum consistent with the extent of the knowledge of probable hazard.
3. A reaction vessel of proper design and metal composition will be used. (Materials Engineering Lab. and the Unfired Pressure Vessel Committee should be consulted.)

CASE HISTORY NO. 929

Acid Residue in Pipe Line

Description: Truck driver was preparing to connect a sulfuric acid tank truck discharge pipe line to a customer's receiving pipe line. The driver pulled the receiving line, which was in a raised position, down to connect it to the truck discharge line. As he pulled the pipe down, residual acid which was still in the raised pipe spilled on the employee's right foot.

The employee washed the acid from his foot, applied his own first-aid, but refused outside medical treatment. He completed his delivery and returned to the plant that evening. Two days later the employee had to be hospitalized for further treatment.

Cause: Failure of another company driver, who had left the receiving pipe line in a raised position, to make sure the pipe was drained before leaving the premises.

Failure of injured driver to inspect the pipe to make sure it was clear before attempting to make his connection.

(If employee had been wearing proper foot wear, such as rubber booties or overshoes, the injury might have been minimized.)

Preventive Measures: Employees have been re-instructed on the need for caution when handling acid pipe lines, including making sure lines have been properly drained in accordance with the Company Motor Vehicle Safety Manual precautions.

The importance of wearing prescribed personal protective equipment when working with corrosive material and receiving immediate medical attention was stressed with all truck drivers.

CASE HISTORY NO. 930

Valve Opened Accidentally--Sprayed with Ammonia

Description: A Field Representative was training a new agent how to load out ammonia from the storage tank to the field tank. The hose he was using was stiff and easily twisted. As the Field Representative attempted to straighten out the hose, it slipped in his hand and the valve struck his face causing the valve to open slightly. A small amount of liquid and vapor ejected from the open valve and struck the employee's face. His injuries consisted of irritation to both eyes, burned mouth, face, neck, shoulders and partial chest.

Cause: It was determined that the accident resulted from failure to remove the vapor and liquid ammonia after previous use. In addition, the handle on the valve had not been sufficiently tightened.

Preventive Measures:

1. Additional training and safety meetings will be held to emphasize this subject.

2. Employees have been instructed to see that all valves are tightly closed when not in use.

3. The supervisor will constantly check to see that protective equipment is worn and every safety precaution observed.

CASE HISTORY NO. 931

Rotameter Rupture

Description: The glass tube of a rotameter, measuring the flow to a kettle of gaseous isobutylene at about atmospheric pressure, broke. As a result of this failure, the glass shield on the rotameter was also cracked but not shattered.

The feed was shut off before sufficient gas could escape to create an explosion hazard.

Cause: It is believed that the breakage occurred as a result of a sudden surge of gas that caused the float to forcibly strike the glass tube. Trouble had been experienced with partial plugging of the feed line system before the rotameter, and it is possible that movement of some of the blocking solids allowed an increase in gas flow.

Preventive Measures: The rotameter will be replaced with an all metal magnetic type.

CASE HISTORY NO. 932

Cleaning Rotameter Glass

Description: The glass of the rotameter needed to be removed for cleaning. This glass is spring loaded. To remove it, it is forced downwards, the top removed from the packing gland and the glass is then removed. All the valves were shut but apparently the trapped SO_2 had vaporized and expanded, causing the pressure to build up. The line had been down for a few days.

Cause: On removing the glass, the pressure released and the SO_2 shot out striking him in the eye. The journeyman who was working here also had put on his safety glasses and suggested to the injured to watch his eyes. Injured was about to put on his glasses but decided to give one more pull on the glass when the accident occurred.

Preventive Measures: This accident would undoubtedly have been prevented had the injured used his eye protection. Instructions were again issued to wear adequate eye protection when checking lines that could be under pressure. Thorough check, such as cracking a union or a flange, to be made on all lines. Employee safety education to be emphasized.

CASE HISTORY NO. 933

Ammonia Hose Rupture

Description: An operator and mechanic were checking operations during the unloading of a tank car of anhydrous ammonia. As they stood on the unloading platform ramp, the liquid unloading hose burst at a point approximately 6 inches from the unloading station coupling, releasing liquid and gaseous ammonia. They immediately walked down the platform stairs and reported the incident. The mechanic then donned a rubber suit and gas mask and turned off the compressor. The foreman, working with the operator and mechanic, was able to secure the liquid and vapor line valves and the valves on the tank car dome.

At the time the hose burst, the ammonia pressure was 175-180 psig, and the car had been unloading intermittently for a period of one and one-half hours. The hose was two-inch steel-reinforced rubber hose designed specifically for anhydrous ammonia service with a maximum working pressure of 350 psig.

The check valves in the tank car and in the liquid line appear to have functioned perfectly.

Cause: Examination of the burst hose indicated that the steel reinforcing braiding had been damaged, so that several of the wires were severed. This overstressed the rubber carcass, resulting in failure.

This hose had last been tested at 350 psig pressure. Since that time, the hose had been removed from its storage location in the chemical area for use in other parts of the plant without approval or knowledge of chemical area supervision. It is suspected that the hose had been crushed and/or exposed to corrosive materials at that time.

Preventive Measures:

1. New corrugated steel hoses covered with braided steel were ordered for both liquid and gaseous ammonia. These hoses are rated at 1200 psig (2 in. liquid hose).

2. Hoses will be tested at 500 psig prior to use for unloading each ammonia tank car.

3. A two-sided shed with roof will be erected over the compressor, valves, and compressor controls to shield the operator on the south and west sides. The north and east sides should remain open to afford emergency egress.

4. The liquid ammonia line and valve will be relocated so that it may be operated from the east side of the compressor. The compressor control support will be relocated to a point 12 inches east of its present location to permit operation of the vapor valve from the east side of the compressor.

CASE HISTORY NO. 934

Molten Sulfur Spray

Description: The sulfur guns were being removed from the furnace in connection with the annual shut-down for maintenance repairs. The sulfur pumps were down, steam had been shut off, and the blower was down in preparation for the removal of sulfur guns.

The steam feed hose was then disconnected and the valve on discharge side of the run was also opened. The repairmen then began to loosen the union on the discharge side of the sulfur gun when the line broke, spraying all three men with hot molten sulfur.

Cause: Upon investigation, it was found that the sulfur gun had a hole in it that allowed molten sulfur to back up into the stream line and become trapped in the steam jacket. With the blower down, and no air going into the furnace, the increased heat caused pressure to build up to the point that it sprayed the trapped sulfur when the line broke.

Preventive Measures: To prevent a recurrence, valves are being installed in all sulfur guns. The valves will be opened prior to any preparatory work for removal of guns which will prevent a pressure build-up of steam or sulfur.

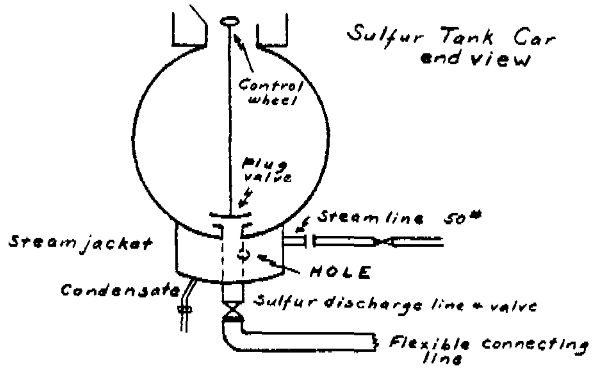
CASE HISTORY NO. 935

Sulfur Tank Car Incident

Description: Maintenance men were preparing to unload a tank car of sulfur when an incident occurred that could have been very serious. They made a steam hook up to the steam jacket in order to free the discharge line of any plug. The discharge valve was opened and this line was drained. After draining, the discharge valve was closed. They then connected the flexible connecting line to the discharge valve. Steam was still on and now ready to open the plug valve. Upon opening the plug valve, hot sulfur (130°C) and steam blew up through tank car opening, spraying catwalk area and running down the tank car. The man on the top and men below miraculously escaped injury.

Cause: A hole had developed in the discharge line inside the steam jacket; and when the plug valve was opened, live steam and sulfur were forced out of the top.

Preventive Measures: In all future unloadings, after the discharge line has been cleared, the steam will be shut off. The discharge valve will also be opened before the plug valve is opened. The vendor has been notified of the bad discharge line and the job procedure has been rewritten to insure the safety of the men.



CASE HISTORY NO. 936

Removal of a Safety Seal Assembly from an Active Vessel under Heat and Vacuum

Description: A pipefitter assigned to the process expansion was instructed and shown by the area production supervisor and the group leader to remove a safety disc from the deactivated #1 still. This disc was to be used on a new vessel being installed.

After supper, about 6:00 p.m., the pipefitter and group leader asked the process foreman if they could remove the designated disc. Permission was given, but it was not until 8:30 p.m. that the pipefitter, thinking he was working on the #1 still as previously shown, actually removed the safety seal assembly from the adjacent active #2 still. A blank was substituted but not securely bolted down. Fortunately, at the time, still #2 was in the process of cooling prior to dropping the residue.

At about 4:00 a.m. the next morning an operator noticed that the safety disc had been removed when, upon purging the vessel with CO_2 prior to dropping the residue, fumes emitted from the loosely connected blank.

Several hazardous conditions could have resulted if the #2 still was not in the cooling phase, such as:

1. Pipefitter could have been hit with hot vapors if #2 still was in stripping phase.

2. Building could have filled with flammable and explosive vapors.

3. Sudden break of vacuum could have caused residue to erupt and spill out through pipe if source of heat was not turned off.

4. Formation of hazardous decomposition products which are potentially explosive upon contact with air.

The foreman, group leader and pipefitter were unaware of the potential hazards involved. The pipefitter admitted that he does not know how he got mixed up. His supervisors say that he (the pipefitter) is a good, stable and dependable worker.

Preventive Measures: 1. Tag all vessels or parts of vessels that are scheduled to be worked on.

2. Identify all vessels clearly.

3. All maintenance foremen should be advised of the potential hazards in every process.

CASE HISTORY NO. 937

Hydrogen Sulfide Cylinder Leak

Description: Hydrogen sulfide leaking from a cylinder caused two minor injuries, but the potential was there for serious trouble. It was necessary to apply warm water to a H_2S cylinder to increase gas flow to a reactor. The cylinder was located on the third floor of an operating building. The valve and flow regulator assembly were under a canvas hood supplied with exhaust ventilation. At the time of the incident, the operator was wearing an air mask, as prescribed, while switching cylinders. After hooking up lines to a fresh cylinder, he tied the water hose to the top of the cylinder, walked to the steam-water mixer, and turned on the cold water. He heard a hissing sound, turned off the water and returned to the cylinder to check. He claimed he smelled H_2S through his mask and ran from the area. When the end of the air line was reached, about 30 feet away, he tore off the mask and continued running towards the exit. He became dizzy and fell against a building column lacerating his ear. He regained his senses quickly and left the floor safely via the center stairway.

When the supervisor was contacted, he called an ambulance for the injured operator, took another operator with him and went to the third floor via the same stairway. When he opened the door the gas odor was very strong. He ran across the floor to where he saw an air mask lying on a drum and put it on, but the air supply had been turned off. He removed the mask and then ran to the platform to turn on the air, began to feel dizzy, turned to the south stairwell and pushed open the window to get fresh air. He fainted momentarily and fell, striking his head on the concrete landing and lacerating his forehead. He recovered quickly and was assisted down the stairs to the ambulance by other men. The gas cylinder was then carried to an adjacent roof by men wearing self contained air masks. With technical assistance, the operation was shut down properly and all personnel accounted for.

Cause: Investigation revealed that the fusible plug had begun to melt, possibly because the initial surge of water to the cylinder was hot. The plug melts at 160-165°F. The very hot water may have been due to a leaky or partially open steam valve at the mixer heating the residual water in the hose used for the cylinder.

The H_2S cylinders have a gold plated rupture disc in contact with the cylinder interior, followed by the fusible plug. This rupture disc was found to be broken and the manufacturer's representative felt it may have been broken before this incident occurred. If the rupture disc had been intact, the gas could not have leaked out.

The leak became very small once the remainder of the fusible element rehardened and the cylinder did not offer any further problems when it was permitted to empty on the roof.

Preventive Measures: To prevent a recurrence, several things are being done.

1. Supervisors and operators are being reinstructed on the need for obtaining emergency respiratory protection before entering contaminated areas.

2. A totally enclosed, ventilated, container will be built to house two H_2S cylinders, capable of handling all the H_2S which could flow from a cylinder.

3. A water collar ring will be used for the hot water which will prevent getting water or steam on the cylinder valve assembly containing the safety devices.

4. A "Strahman" type steam-water mixer will be provided that does not permit flow of steam until there is a flow of water.

CASE HISTORY NO. 938

Sulfur Tank Car Incident

Description: A pipefitter scalded several fingers of both hands and his chest and dislocated one ankle. Shielded safety spectacles protected his eyes from the hot water. He will lose at least a month.

After shutting down a steam line to repair a small leak he unbolted a flange connection and spread the flanges preparatory to replacing that section of pipe. Several minutes later hot condensate poured out of the opening onto his fingers, chest and face, so he jumped or fell from the third or fourth rung of the ladder and turned one ankle as he landed on metal grating. Fellow workers immediately applied cold wet cloths to the burned fingers while awaiting the plant ambulance.

Cause: Condensate in a higher run of pipe probably did not run out until enough air had gurgled through it to break the vacuum holding it, so this delayed gush of hot water was totally unexpected as the line had drained minutes earlier at the parted flange connection.

Preventive Measures: Bleed valves are being installed at high points of steam runs to facilitate complete drainage by eliminating air locks which might hold back condensate. Work permits will be more specifically worded and followed to include foreseeable hazards.

CASE HISTORY NO. 939

Handling a Flammable Solvent

Description: An employee was preparing to load acid into a trailer. The hose was in the tank and water was being loaded. When he put the metal gauge stick into the tank, an explosion occurred. The employee received moderate to severe burns on his face and right leg.

Cause:

1. There was approximately one-half barrel of flammable solvent and diesel fuel mixture in the trailer tank. An employee who had used the trailer the day before had failed to flush the tank.

2. The employee dropping a metal gauge stick into a tank containing a flammable mixture.

Preventive Measures: It has been determined that this flammable solvent can be pumped safely if properly handled. Therefore, any future pumping of this mixture must be approved by the Safety Department so adequate safety measures can be set up.

CASE HISTORY NO. 940

Making Adjustments on a Process Line in Operation

Description: This accident occurred in the salt removal portion of the Hydrazine Production Plant. The specific equipment involved was an 8 inch sight glass in the line from the slurry thickener to the mother liquor tank. There had been repeated instances of the 8 inch Pyrex view plate cracking due to the difficulty in adjusting the four bolts on the glass support ring. There was also a tendency for the highly alkaline mother liquor to etch the back of the glass making viewing difficult.

Approximately forty-five days before the accident, a piece of 1/4 inch Plexiglass was substituted for the 3/4 inch eight-inch diameter Pyrex glass. It was found that the plastic would not crack and was not affected chemically by the solution. Since this system normally operates under little or no pressure at this point, it was felt that the substitution was justified.

On the day of the accident, the line below the sight glass became blocked with salt as it had in the past. The sight glass became filled with liquor and the overflow from the thickener was stopped. The employee, believing that the line was under vacuum rather than pressure, attempted to vent the line by loosening the two top bolts of the sight glass support ring. As soon as the ring was loosened, the plastic which heated beyond its softening point, pulled from beneath the flange and then broke. The hot liquor sprayed forcefully onto the employee's face and body.

Cause: Three basic things were involved which contributed to or caused this accident.

1. Poor judgment on the part of supervision to substitute material in the salt removal system which could not tolerate the 255°F liquor temperature.

2. Unsafe act on the part of the experienced foreman in making an adjustment to a process line while in operation.

3. The flaw in the process which would allow a portion of the system which would normally be at atmospheric pressure to become pressurized to an estimated 30 to 35 psig.

The employee's injuries consisted of first, second and third degree burns to approximately 20% of body surface including face. Also, burns to cornea of both eyes.

Preventive Measures: In order to eliminate the problem of vapor lock in this mother liquor line, a condenser had already been ordered and was due for delivery five days after the accident occurred. This unit will be installed and will eliminate such difficulty in the future. The sight glass will be modified to reduce the view port to 5 inches which should eliminate the breaking problem experienced in the past. It is possible that a thick Plexiglass plate will be used if tests indicate it can survive the designed capacity of the sight glass unit.

CASE HISTORY NO. 941

Help the Helper

Description: An operator and helper with only a month's service had been assigned the job of making up a charge of catalyst. While the operator was away from the area, the helper noticed liquid leaking overhead. When he reached the second floor, he saw vapors and liquids coming out from around the tank manhole. As he attempted to stop the leak by tightening up on one of the two bolt clamps, the clamp broke and the manhole cover was blown off. He was found semiconscious a few minutes later by the employee assigned to the panel control in a nearby building who had noticed a sharp drop in the level of the liquid in the tank and had come to investigate when he could not contact the helper on the PA system.

Cause: Incorrect valve adjustment. Investigation showed that the valves on the overflow line were closed.

Preventive Measures: The importance of training and guidance given to helpers and new will be re-stressed to all employees.

CASE HISTORY NO. 942

Unauthorized Operation of Tow Tractor--Fatal

Description: A sandblast leadman was fatally injured while operating a 4,000-pound capacity tow tractor in a non-operating storage warehouse. He left his work area to obtain extra glass face pieces for sandblast helmets. He entered an adjacent non-operating warehouse, and for reasons unknown, proceeded to operate an electric tow tractor. While operating the tractor in the poorly-illuminated warehouse, he turned sharply to the left and was pinned between a depressed gun tube of an anti-tank vehicle and the rear motor frame of the tractor. The front part of the tractor, from the driver's seat forward, passed under the gun tube. Adequate clearance, however, did not exist to permit the raised rear part of the tractor and operator's body to pass under the gun tube. The operator apparently was unable to stop the tractor, or did not see the gun tube. Death resulted from compression of the chest area.

Cause:

1. The employee was not experienced in the operation of this type.
2. The employee failed to see the gun tube due to poor illumination.
3. The operator attempted to make a sharp left turn at an excessive speed and lost control of the tractor.

Investigation of the accident revealed that the fatally injured employee did not possess an operator's permit. His position did not require that he operate a powered industrial truck. Examination of tire skid marks indicated that the tractor was started with the motor excessively accelerated, causing the wheels to spin on the warehouse floor. The tire marks further indicated that the operator attempted to make a sharp left turn while traveling too fast. At the time of the accident, the building was not in use and the overhead lights were not turned on. This condition resulted in poor illumination. Several hours prior to the accident, the employee involved in the accident had questioned a licensed operator concerning the operating controls of a tow tractor. He had also operated a piece of materials-handling equipment in the building where sandblast operations were in progress.

Preventive Measures:

1. Only authorized personnel shall be permitted to operate powered materials-handling equipment.
2. Operators shall be carefully selected, thoroughly trained, and required to pass an operating test before they are permitted to operate powered materials-handling equipment.
3. All prospective operators should undergo a physical and mental examination, given by a qualified medical examiner, to determine that they are physically capable of performing their duties.

CASE HISTORY NO. 943

Contact Lenses and Caustic Soda--Near Miss

Recently an employee was splashed in both eyes with caustic soda but fortunately did not receive serious burns.

He is a 20-year-old male and had been employed in the plant for only three months. About three weeks before the injury he had obtained contact lenses and was warned even by his own physician not to wear them around chemicals. However, he had to build up time to tolerate them and decided to wear them in the plant. This was only the second time he had worn them on the job. In addition to the contact lenses he was wearing plano-type safety spectacles with side shields.

However, as he was holding up soda press plates in the soda room and closed the plates, some soda splashed into both eyes under the spectacles. He did not wash his eyes at the eye wash fountain for fear of losing his contact lenses and when he arrived many minutes later at the dispensary the lenses were still in place and still no water had been placed in his eyes. After emergency treatment and referral to an outside physician he was returned to work without serious burns.

This can only serve to illustrate again the danger of wearing contact lenses when working around chemicals.

Even more important, employees must be trained and retrained in the great urgency to immediately flush eyes with copious quantities of water when they get any sort of chemical in them. In the case of caustic soda, we cannot overemphasize this point.

CASE HISTORY NO. 944

Introduction of Water to a Sulfonation Reaction Resulted in Violent Decomposition

Description: Mononitro benzene was being sulfonated with oleum in a 750 gallon cast iron reactor having an open manhole. A leak in the internal cooling coil permitted water to enter the reactor. Reaction between water and oleum raised the temperature from 110° to above 150°C. An explosion resulted damaging the top of the reactor. The reaction mass ended up outside and was mainly foamed carbon.

A sample taken just before the explosion analyzed 11 percent water; all other components were normal. The rest of the sample was subjected to 165°C. for one half hour and with the same result as the plant batch. A laboratory mix containing no water was found to decompose at 190°C.

Cause: Water from the leaking cooling coil reacted with the oleum.

Preventive Measures: Coil will be replaced in the future on indication of serious reduction in wall thickness. An emergency dump line is to be installed to an outside sewer.

CASE HISTORY NO. 945

Bromine Burn--Another Valve Incident

Description: Mechanics started on necessary repairs to put the bromine system in a building back into service. The system had been shut down for several months, and it was necessary to replace gaskets, vent lines, valves, and thoroughly check out the system. Mechanics were closely observed while cutting into system by supervision, and everyone was made aware of hazards when handling bromine. Plastic gloves and gas masks were worn while initially cutting into lines. On the morning of the accident, two pipefitters were assigned to check out the piping system for blowing bromine from tank cars and to replace gaskets and necessary fittings and valves. As the system was already disconnected in several locations, gas masks were put aside. Shortly after lunch, they were replacing pressure reducing valve and noticed 1/2 inch ell was loose. In order to tighten this ell, it was necessary (because of clearance from wall) to remove the needle valve. The injured started to remove this valve, loosening it very carefully. When the valve was nearly off, he wiggled it but seeing no evidence of any liquid or fumes coming from the connection, removed it. Immediately, a small portion of bromine trapped from top of needle valve to the ell spilled out, burning him on the forearm, wrist and hand and splashing over his clothing. Another fitter working nearby on vent system suffered a minor burn on his leg.

Cause:

1. Nitrogen pumping system was not considered a hazardous part of the system. (No bromine was supposed to be present at this point.)
2. Some items of protective equipment were not used after initial break-in.
3. Gloves worn on this job did not adequately protect hand and wrist.
4. Piping was installed so that natural pocket for material was formed.
5. There is no written procedure for shutdown of this system.
6. There is no positive method of completely purging system of bromine.

Preventive Measures:

1. Revise bromine piping so that 1/2 inch needle valve and regulating valve are above straight section. Revise nitrogen inlet section of piping so that any liquid will drain east towards tank car.
2. Install flange covers on all lines which carry liquid bromine.
3. Write down specific instructions for shutting down bromine system at the end of a run. Consider purging lines with nitrogen or some other inert medium.

4. When working on the bromine system, a Santosite-Soda ash (50:50 mixture) solution to be provided at all times to neutralize any spills in the area. Water in copious quantities should be readily available for skin contact.

5. Minimum protective equipment when working on any part of the bromine system is: gas mask, rubber gloves (shoulder length), and rubber suit. A full rubber suit and an air hood with an outside air supply is strongly advised, when blockages occur and pressure cannot be released. The bromine piping is considered to be the entire system, from the nitrogen cylinder – to the tank car – to the reactor – to the caustic scrubber – to the atmospheric vent.

6. All department supervision review the protective equipment requirements for similar hazards in their respective operations.

7. All maintenance supervisors and foremen re-emphasize the fact that hazardous systems are still hazardous even after initial break-in, and safety precautions should not be relaxed at any time.

8. All departments review this accident at the next safety meeting.

CASE HISTORY NO. 946

Sulfuric Acid Burn-- Still Another Valve Incident

Description: A 1/2 inch control valve regulating the flow of sulfuric acid to the demineralized water system, had been removed from the system for repair.

It had been flushed out with water several times before attempting the repair. While removing the packing from the valve stuffing box, foreign material from the valve went in the injured's right eye.

Cause: Sulfuric acid had been trapped. It released when the packing was being removed from the valve stuffing box.

Preventive Measures: Wear eye protection. Treat valves as product traps (see Case History No. 864 also).

CASE HISTORY NO. 947

Mild Steel Fails in Cryogenic Service

Description: Rupture of an ammonia cylinder resulted in moderate injury to one man and relatively light damage.

It was accepted procedure to fill a 2 liter cylinder from large ammonia cylinders by placing it in a bath of dry ice and acetone. This was done a few hours before the rupture and the man stated that the correct weight of 1 Kg was charged. The cylinder lay in the walk-in hood of a production laboratory and no one was working in the hood when the steel failed with a clean split up the entire length of the cylinder. A bottle containing PCl_3 and one containing chlorosulfonic acid – both stored in the hood – broke. A thick cloud of fumes resulted. Two members of the fire brigade, wearing air masks, determined that there was no fire and it was decided to spray water on the floor to neutralize the reaction.

As soon as this was started, another explosion occurred and a small fire resulted which was quickly extinguished. The sprinklers in the hood were operating from the time of the cylinder rupture. The second explosion was caused by exposing about 520 gms of sodium which was stored in a bottle in the hood, to the water spray.

The injured man was a technician who was working next to the hood. He suffered burns of the feet and a hand and was put under a safety shower as soon as possible. He lost some time from work but the burns were not considered very serious. Damage was limited primarily to the hood interior.

Cause: In discussions with gas cylinder suppliers, they felt that subjecting the steel to acetone-dry ice temperatures of -70°C. would cause it to become brittle and fail under nominal pressures. The cylinder was tested two years ago at 225 atmospheres.

Preventive Measures: It is best to leave cylinder filling to suppliers who are expert in this art. Where we must fill cylinders, alternative approved methods are available. Storage of chemicals in a working hood should be banned.

CASE HISTORY NO. 948

Explosion of Pyrotechnic Flare During Testing

Description: While performing routine candlepower measurements of a pyrotechnic flare, a project engineer was fatally injured. The injury occurred from a door blown open by unexpected "explosion" of the flare. The operation was routine and all the safety precautions believed to be adequate had been taken. The incident was completely unforeseen and without precedence. On the day of the accident, the project engineer had delivered two flares to the photometric tunnel for candlepower and burning time measurements. The flare was fused as usual in the tunnel with loose starter mixture, firecracker use and an electric match. The terminals of the electric match were connected while the flare was sitting on the test stand. The project engineer and tunnel operator went to the instrumentation room to ignite and record the data from the burning flare. The door was closed and bolted with a steel bar across the entire width. The common practice used for initiation of flares for candlepower measurements in the photometric tunnel employed the use of a dry cell battery. The first try at initiation failed. The project engineer waited approximately 5 minutes and then entered the tunnel to determine the cause. Upon inspection of the flare, no apparent cause for nonignition was noted. It was concluded that the dry cell was dead. A new dry cell was obtained and upon ignition, the flare exploded, collapsing the walls of the tunnel. The project engineer was standing near the edge of the door in the instrumentation room. The shock wave (or sudden increase in pressure) sprang the lock on the door. The swinging door struck the project engineer on the forehead with sufficient force to result in a fatal injury.

Cause: The extensive force generated by the deflagration of this flare had never previously been observed during local burning tests nor was it known of anything comparable to this being recorded at any other activity. An intensive investigation was conducted to determine cause for explosion of this flare. A review of the test work prior to the testing of the final flare failed to indicate that an explosive type action could be expected. Laboratory experimentation failed to uncover any significant factors which would tend to indicate detonation of the material (magnesium, sodium nitrate and laminac). The conclusion was ultimately reached that the explosion of the flare must have been caused by the physical makeup of the unit. It was hypothesized that the explosion was caused by the initial flame front traveling down either the sides of the case, down the center pin or a combination of both of these. As the flame front moved rapidly toward the base of the flare, pressure rapidly increased, thereby causing a rapid increase in the burning rate and in chain reaction fashion burning so rapidly as to cause the pressure to increase sufficiently rapidly to burst the sidewalls of the case before the composition could be ejected from the case. A limited number of tests were conducted with experimental units to verify or disprove this hypothesis and these tests strongly indicate that the hypothesis is correct. The results tend to show that the center stud and the fact that the case was not lined did not necessarily by themselves provide the conditions for deflagration but a combination of these factors with others (such as rapidly burning composition, fine particle magnesium, a low percentage binder and relatively low pressing pressure) led to the conditions which produced the explosive results.

Preventive Measures:

1. Use of the center stud is being eliminated wherever practical.
2. All steel cases will be lined even though they are being used for exploratory type work. (It has been found many times before that the flare case must be lined in order to provide proper burning at reduced temperature.)
3. The pyrotechnic tunnel was not designed to provide for an explosion. The walls surrounding the burning area in photometric tunnels should be designed for this potential with blowout walls, cheap in construction and readily replaceable.

CASE HISTORY NO. 949

Did Patch Scale-up Cause Blow?

Description: An explosion occurred in a lead azide jelly bag mixing unit at approximately 1:00 p.m. during blending operations at a mix house. A chemical worker had charged the jelly bag with 7 pounds of lead azide and 1/2% calcium stearate, using the remote control dumping device. He had activated the agitating motor and had left the building to attend to an adjacent disposal vat. A second chemical worker remained in the control room to monitor the mixing unit and to dump the batch when the counter showed the blending cycle to be completed. The mixing cycle was about 20% complete when the explosion occurred. No personnel were injured. Weather conditions outside the building were warm, partly cloudy, humid and virtually no wind. Temperature was 91°F. The humidity of the building was controlled at 70%. The mix building was wood frame construction, with blowout walls and light roof. The entire portion of the building behind the reinforced concrete barricading wall was demolished (the two side walls, back wall and roof were shattered); a small crack was in evidence in the concrete barricading wall extending from the top of the entrance doorway of the blending room to the top of the wall; water and electric lines were damaged and require replacement; jelly bag blending and screening unit were destroyed.

Cause: Cause of the explosion unknown. No abnormal conditions had been noted by either operator in the blending building or the surrounding area. Equipment and static grounds in building were checked approximately 6 weeks prior to date of incident and no defective conditions were noted. The absence of explosions during the mixing of 300 batches of lead azide without calcium stearate prior to the date the incident occurred might indicate process change might have contributed to the explosion. Process change included increase of batch size from 3-1/2 pounds to 7 pounds; the addition of 1/2% calcium stearate; the screening through smaller mesh screen.

Preventive Measures: Since the cause of the explosion could not be determined, all changes in the process made on the day the incident occurred will be eliminated. These are:

1. Discontinue use of calcium stearate.
2. Reduce batch size to 5 pounds.
3. Change size of screen from 108 to 50 mesh or less.

CASE HISTORY NO. 950

Heat Exchanger

Description: A mechanic was working in the convertor bay at the ammonia plant helping to remove the tube bundle from the amine heat exchanger. The outer shell rolled over, catching his leg between the shell and the cylinder when an attempt was made to pull the tube bundle from the shell.

Cause: Improper job set-up; neither end of the exchanger was secured.

Preventive Measures: Both ends of the shell will be secured in the future before the tube bundle is pulled from the shell.

CASE HISTORY NO. 951

Ammonia Sprayed from Pump-- Two Men Burned

Description: Two employees were changing a valve on a pump. After the inlet and discharge valves were closed to isolate the pump, the men proceeded to pull the cover plate. As the cover plate came loose, ammonia sprayed on the men. One employee was burned on the shoulder and the other was burned on the neck.

Cause:
1. The pump contained residual pressure.
2. One of the men was not wearing a face shield.
3. The men failed to check the pressure in the pump.

Preventive Measures:
1. A vent line is being installed on the discharge line of the pump to insure venting of residual pressure.
2. To make venting more positive and to insure that no liquid ammonia remains, the pump will run idle to vaporize the material while it is being vented.
3. Face shields will be mandatory to supplement safety glasses with side shields.

CASE HISTORY NO. 952

Are Instructions Complete?

Description: An employee was using a spud to clean solidified material from the outside of a flaker drum. As he was chipping a build-up of material, the spud went through an opening in the flaker hood. Manhole cover bolts on the revolving drum caught the blade end of the spud, causing the handle to come down and strike the employee on the nose. He received a severe laceration of the entire length of the nose.

Cause:
1. The opening on the flaker hood was originally designed for a water wash clean out, but was no longer necessary.
2. The employee used a spud to clean the flaker hood while the flaker was in operation.
3. The projections on the end of the flaker are bolts that hold the manhole cover in place.
4. The hook on the spud handle was designed to prevent the spud from slipping in the operator's hands.

Preventive Measures:
1. An operating manual (with safety considerations) will be written to cover this job, with regular reviews and up-dating procedures established.
2. The opening in the flaker hood has been covered.
3. The side knives will be properly adjusted to minimize material build-up on the end of the drum and dripping on the hood.
4. The handle on the spud will be redesigned.

CASE HISTORY NO. 953

Cylinder Refilling

Description: In the set-up in the safety department for refilling Pneolator Oxygen cylinders, (21 cubic ft. capacity cylinders) the larger Oxygen cylinders from the supplier are used. Such cylinders are located on the outside of the building and connected by a 3000 lb. tested stainless steel tubing running through the wall and to directly over a work bench, a distance of approximately 15 feet to the valve. The regulator is attached to the valve at this point and the regulator that had previously been used was approximately 6-1/2 years old. The gauges were not operating properly and it was decided that a new regulator would replace the older one.

A new regulator was ordered from the manufacturer locally and when the same arrived was taken directly from the packing box in which it arrived and placed on the valve. One hour previous to installation of the new regulator, the entire line leading from the large cylinder located outside the building was blown out as a precaution and to eliminate any foreign materials. This was done by opening the valve on the large oxygen cylinder and blowing out same.

When the new regulator was tightened and in place, the gauge on the outside cylinder was opened slowly and oxygen was permitted to flow through the line and into the valve located inside the building which was closed. The inside valve was opened slowly and the gauge on the high pressure side of the regulator showed a pressure of between 2000 and 2100 lbs. on the gauge. This was permitted to stand this way for approximately 1 minute at which time the screw valve was turned to permit oxygen to flow to the low pressure side of the regulator. When the screw valve had been turned clockwise about 1/4 turn, a terrific explosion occurred and belching flames and molten metal spewed over the immediate area. Molten metal from three holes in the regulator was found as far away as twenty feet.

A pad of unused matches with the cover closed was lying on a table approximately 8 feet from the explosion. Investigation revealed that all had been ignited within the pad and the cover was not even scorched.

The safety director was turning the screw valve on the regulator and standing approximately 5 degrees to the left of center of the regulator. The explosion blew one hole on the left side of the bell housing, another on the right and downward and another in the rear at the bottom of the flange. He received second and third degree burns on the right thumb and index fingers as this was the hand being used to turn the screw valve. His clothing was burned from hot metal.

A safety inspector who had been outside to turn the valve on the large oxygen cylinder had just walked in the door approximately fifteen feet away from the regulator when the explosion occurred. He was blown back out the door approximately 8 feet.

(It might be well to note that nothing was attached to the outlet line of the regulator at the time of the incident inasmuch as they were only checking to see if the regulator was satisfactory.)

Cause: It is probable that either grease or oil had been permitted to enter the inside of the regulator accounting for the explosion.

Preventive Measures: A testing program has been introduced for all regulators, new or old. They will be placed in position on the line and oxygen will be fed from outside the building with no personnel permitted inside while the test is occurring.

CASE HISTORY NO. 954

Gas Explosion

Description: The desired temperature of a sulfuric burner in a sulfuric acid plant had been reached (1800^{o}F) by burning of a propane gas mixture. The gas burning equipment then was shut down by pushing two electrical control buttons which closed two 2-1/2 inch and two 1/2 inch electrically operated valves. Following the closing of the gas valves, the main air blower that supplied combustion air for the gas was shut down.

Approximately ten minutes after the burner had been shut down, two men were requested to remove a blind flange from a 4 inch nozzle on the vaporizer cover. The vaporizer is a tank 6 feet in diameter x 8 feet high located adjacent to the sulfur burner and connected by an 8 inch pipe. One employee was standing on top of the vaporizer and the other employee (injured) was standing on a stepladder alongside of the tank. His face was about level with the 4 inch nozzle. There was a sudden explosion and a flash of flame came out of the nozzle burning the injured on the face, neck and upper chest. In trying to get away, he fell and lacerated his knee.

Cause: Investigation revealed that failure to close the primary gas cocks was the cause of the accident. The Investigation Committee believes the explosion was caused by gas leaking past one or more of the electrically operated shut-off valves. A hot brick surface was present and when sufficient gas accumulated to produce a combustible mixture, it exploded.

Preventive Measures: A thorough review of operating techniques with all operators, particularly infrequent start-up and shutdown practices.

CASE HISTORY NO. 955

Inhalation of Chlorine Gas

Description: An employee was engaged in charging chlorine cylinders. This involves the connecting of a full one-ton cylinder to the distribution system, and disconnecting the empty cylinder. Present practice has been to have cannister type gas masks at the job location, but not to wear them. In this case, the gas masks were present, but were not being worn.

The chlorine cylinder station is located outside. The employee, who had performed this job many times, had checked the isolating valve to see that it was closed tight and then proceeded to remove the 3/4 inch steel pipe plug from the free end of a three foot length of 5/16 inch copper tubing. When the plug became loose, a quantity of chlorine gas was released and inhaled by the employee.

Cause: Investigation revealed that a procedure was written several years ago that required the wearing of a gas mask while performing this operation, but the short cut of having it present but not wearing it has been substituted.

Preventive Measures: The procedure will be reviewed with supervision and a gas mask will be worn by persons performing this operation.

CASE HISTORY NO. 956

Acid Sprayed While Thawing Line

Description: An employee was heating a cast iron acid line containing 99% sulfuric acid to thaw the line. While trying to establish flow by heating the line, the acid sprayed out from a crack in the line into the employee's face. The employee's injuries consisted of second degree acid burns about the face and hairline, neck, and forehead. In addition, he sustained severe corneal burns to both eyes.

Cause: Investigation revealed that the cast iron pipe cracked from heating the line. The employee was wearing safety glasses but should have been wearing safety goggles or a face shield.

Preventive Measures: Acid line will be steam traced and insulated to prevent freezing. Employees have been instructed in the use of protective clothing, face shields and safety goggles.

CASE HISTORY NO. 957

Beaker Containing Lead Styphnate Exploded

Description: An employee was removing a beaker of lead styphnate (lead 2,4,6-trinitroresorcinate) from a laboratory oven. He grasped the beaker with his left hand and, as he turned, he apparently bumped the beaker on the side or bottom of the oven opening and a detonation occurred. The detonation propagated to the other two beakers in the oven and all three detonated. The man's injuries consisted of perforated colon, lacerations to arms, abdomen and hands and perforated ear.

Cause: The causes of the accident were:

1. Inadvertent mishandling of explosives.
2. Drying explosives in glass beakers.
3. Possibility of detonation from impact during handling while hot and dry.
4. Flaw in beaker from thermo effects.

Preventive Measures:

1. All ovens shall be equipped with upper limit temperature control and grounded.
2. Drying lead styphnate for the purpose of determining the average granulation size weight will be accomplished by weighing in water using a pycnometer.
3. Handling of dry explosives will be eliminated whenever possible and use of glassware will be minimized.

CASE HISTORY NO. 958

Possible Static Electricity Flashes Flammable Vapors

Description: An employee was renewing the filter "heel" on the screen of a centrifuge. The old "heel" powder had been scraped off and the screen flushed with a vehicle. The fresh powder was stored in a leverpak with a polyethylene drum liner. Because the drum was nearly empty, the employee dumped the powder directly from the liner into the centrifuge. It was at this time that a flash occurred. The employee received minor and moderate burns to both arms, face, ears, and neck. Two maintenance employees who were standing by to close up the centrifuge received moderate burns on their arms as they assisted the employee from the area.

Cause:

1. High level of fumes inherent in process.
2. Possible static charge created by powder flowing from the polyethylene bag.

Preventive Measures:

1. Operator to wear aluminized jacket and hood with air supply.
2. Flushing with vehicle will be discontinued.
3. A grounded aluminum scoop will be used to apply fresh powder.
4. Additional grounding of centrifuge to be provided.
5. Use of polyethylene drum liners will be discontinued.
6. Block valves to be installed on centrifuge to limit vehicle fumes.

CASE HISTORY NO. 959

Ammonia--Leaking Control Valve

Description: Employees were starting up a granulation operation after a four hour shutdown. They were in the plant control room. As the granulator started rotating, liquid ammonia, which had leaked past the closed valves, vaporized rapidly, overtaxed the fume collecting system and billowed out. The doors at the discharge end of the granulator were open for observation, and the ammonia vapors flowed out and into the control room just as the employees were leaving to inspect the granulator product exit. The employees were forced to retreat and leave the room through an exit behind the control panel, which exposed them again to heavy ammonia concentrations. One employee was hospitalized.

Cause: Ammonia which leaked past two closed manual block valves, and a closed automatic control valve, did not vaporize because it was trapped by crusted material or because the sparger nozzles were plugged.

Also, the granulator fume collection duct and the duct entering the primary scrubber were partially blocked.

(Note: The vapors discharged so rapidly, employees did not have time to don protective masks and leave the control room which is in direct line with the granulator discharge. The door in front made it necessary for the employees to exit from the room via a door behind the control panel which opens alongside the granulator.)

Preventive Measures: The leaking control valve has been repaired and the two block valves are being replaced.

The granulator fume system will be cleaned regularly and the plant will not be operated unless there is sufficient draft on the fume collection system. Also, a spray has been installed in the duct entering the primary scrubber to prevent blockage at this point.

A door is being installed at one end of the control room to provide another emergency exit.

CASE HISTORY NO. 960

Explosion--Sight Glass Failure

Description: Trying to repair a leaky sight glass on a vessel under pressure was the primary cause for a chemical plant explosion and fire that resulted in 7 deaths, 2 critical injuries and property damage exceeding $4 million.

The 85 ft. x 85 ft. building with drying and packaging area attached contained 20 – 2,000-gallon reactors used in the manufacture of polyvinyl chloride (PVC). All electrical equipment was explosion-proof and the building was ventilated at 20 air changes an hour.

One reactor had trouble with the 6 inch sight glass which had a light above it. The lead and asbestos gasket and sight glass were replaced and the vessel put on stream. The foreman noted that at 140°F. and 140 psig, the system was tight, but while the maintenance men were in the building to repair a valve on another reactor, they were asked to check the sight glass. A small leak was observed and a maintenance man tightened the nuts with an open end wrench (not a torque wrench). On the second round of tightening, a one inch ribbon stream of water and vinyl chloride suddenly shot out and knocked the man down. He was bleeding from the face and escorted out of the building. Regular emergency procedures were started immediately, e.g., windows and doors were opened, steam to reactor shut, additions stopped, and the manual vent to the reactor opened.

An operator was overcome by vapors and carried out. Five minutes later a tremendous explosion occurred, ripping the building to pieces. The contents of 18 reactors were dumped but there was very little fire in the building. The explosion wrecked the sprinkler system and the Post Indicator Valve could not be reached. Pressure dropped to zero in critical locations. There evidently wasn't a sprinkler line loop on this area. A warehouse, laboratory and office building 150 ft. x 800 ft., was 60 feet south of the building. A wall was blown down, several small fires started and propagated along the roof. The roof caved in and the building burned several days, to complete destruction. The sprinkler pressure was zero in this area. The boiler and maintenance building 80 feet to the north, was extensively damaged and other surrounding buildings also were damaged to varying degrees. Windows in homes were shattered and some homes evacuated.

Of the dead, one was found in the dryer room attached to the building. Four bodies were found outside, between the building and the warehouse, indicating that conditions had changed from emergency to evacuation within a five minute period. One fatality occurred in the boiler room, 80 - 100 feet away.

Cause: The investigators feel that the 6-inch sight glass shattered completely, causing a sudden build-up of flammable vinyl vapors which found an unknown source of ignition. Possibly glass fragments broke the ceiling lights.

CASE HISTORY NO. 961

Plugged Transfer Line

Description: An operational difficulty, poor communications, and faulty judgment resulted in a steam burn and 2 days of lost time. A section of transfer line between 4 stills became plugged with tars and could not be unplugged with solvent or nitrogen. A cap on a branch section of piping was removed and high pressure steam connected. At the sections of the line that were free, valves were set to permit condensate to bleed to the floor. The section leading in the other direction was plugged and valves to these stills opened wide. At shift change the outgoing supervisor informed the incoming supervisor of the conditions and explained in detail the positions of the valves on the transfer line. Without direction from either supervisor, and without notifying the supervisors, an incoming operator noticed the condensate coming from the end of a bonded hose and shut 3 valves on this system. The supervisor went to check about 10 minutes later, saw only drops of condensate coming from the bonded hose and opened a plug cock on this line to check steam conditions. As soon as the condensate drained out, a sudden gush of steam caused the unsecured hose to whip and steam contacted his legs. He applied cold water and was transported to Plant Health.

Preventive Measures: Use of high pressure steam for this purpose is very hazardous. A memo from the plant management has been issued, re-emphasizing to supervision that it should not be done. The operator obviously should not have touched the valves without finding out why the condensate was flowing. The department head has instructed his supervisors to transmit information on unusual conditions or procedures by personally visiting the site. Flexible hose should not be permitted to hang loose on any system that can be under pressure. Either detach it completely or secure it and direct it away from personnel. Plant management has re-emphasized this directive as well.

CASE HISTORY NO. 962

Phosphoric Acid--Corroded Valve

Description: Crude 54% phosphoric acid was being pumped from tank car storage to the granulation process on a continuous basis during manufacture of a fertilizer grade requiring its use.

A 2 inch Keystone butterfly-type valve, located 8 feet above ground at the acid pump station beside the tank car, failed, allowing phosphoric acid to escape. The valve stem blew out and acid sprayed in a stream for a distance of about 50 feet, passing directly over the head of the maintenance foreman who was inspecting the pump at that moment. Aside from a few drops which fell on his clothing, none of the acid struck the foreman and he escaped without injury.

Examination of the butterfly closure of the valve showed it to be badly corroded. The four internal cap screws which attach the valve stem to the butterfly had fallen out because of the corrosion, leaving the stem free to be blown out by line pressure.

Cause: A vertical heat exchanger is located on the phosphoric acid line after the pump so that the acid can be heated to reduce viscosity in cold weather or for increased flow rates. The system is equipped with a bypass line around the heat exchanger. The valve in question is located immediately after the heat exchanger and can be closed to stop flow through that side. There was evidence that faulty operation of automatic thermal controls was permitting steam leakage which caused overheating of residue acid in the heat exchanger when that unit was being by-passed. The continual presence of hot acid next to the valve caused accelerated corrosion over several months of service. The valve parts were made of stainless steel, rated one of the best materials for phosphoric acid service. Similar valves elsewhere in the line which had not been subjected to such hot acid were found to be in excellent condition.

Maintenance personnel had been checking pump flow just prior to the incident. It is believed that the resulting minor pressure variations triggered the final collapse of the valve.

Preventive Measures: 1. Eliminate the valve by removing the by-pass and sending all acid through the heat exchanger side whether or not heating is required.

2. Inspect the pump and remainder of fittings in the line.

3. Establish a more complete inspection of the system.

4. Consider modification or replacement of the present type of valve.

5. Consider the use of other materials of construction for the pump, valves and lines.

6. Use a heat exchanger designed to prevent retention of acid during shut-down, etc.

7. Use annealed and quenched machined parts. These can be so specified on the purchase order for the valve.

CASE HISTORY NO. 963

Overheating Causes Explosion Inside Raymond Mill

Description: An explosion occurred in the Raymond Mill equipment while compounding resin. Operating records and personnel indicated operations appeared to be normal up to the time of the explosion. The venting of the explosion to the atmosphere was witnessed by one of the production laborers returning from dinner break. He ran into the building and pulled the manual trip on the CO_2 fire protection system inside the door, while sounding the alarm to the mill operator. The mill operator, unaware of the explosion, shut down the equipment by opening the electrical breakers on the mill and auxiliaries. This prompt emergency action by operating personnel, in the absence of the automatic operation of the CO_2 protection system, may have reduced the seriousness of the incident.

Cause: 1. In our examination, we found several cubic feet of fused and decomposed one-stage resin in two places in the air system. This one-stage resin had been subjected to excessive temperature and the material had melted and charred.

2. Investigation showed that the material in the mill was abnormally hot when the mill was opened, and the air passages around the roller section were packed so firmly with hot glazed material that the material had to be rodded loose to effect cleaning. This was caused by the long cycles required with a 6000 lb. batch to make the very fine grind on the resin compound. The mill had been grinding five hours on this batch when the explosion occurred.

3. Investigation also showed that the mill was abnormally overloaded, which in itself gives longer cycles and high temperatures. The packed material in the air passages was six to eight inches thick. This condition was explained by a split rubber hose at the mill on the high vacuum lead to the controller feed manometer.

4. About 300,000 pounds of material had been ground in the mill since the last one-stage resin, but it wasn't until three consecutive batches of the compounded resin were ground that trouble occurred. Only then were excessive temperatures finally imposed upon the one-stage resin laying in the system and the one-stage material began to char and burn. This resulted in an explosion of minor nature.

5. The present CO_2 fire protection system is built to allow temperature rises due to ambient temperature changes and/or normal grinding heat. Because of our means of ignition in this explosion, the heat rise was probably within the allowable temperature rise limits and automatic functioning of CO_2 protection did not occur. The committee also feels that after several days of operation, the detection heads will be so crusted with compound that they might be less sensitive to heat and/or weak pressure.

Preventive Measures: 1. Revise the air conveying system to eliminate ledges and shelves where resin compound can settle, specifically the pipe on the mill fan inlet and the pipes at the top of the cyclone separator. If this is impossible, provide cleanout doors of other means to remove these solids during cleanups.

2. All operators should be reinstructed and become completely familiar with the layout and operation of all facets of the CO_2 fire protection system. This should include detection heads, automatic and manual tripping, electrical alarm tie-ins, spare CO_2 cylinder bank and shut-down devices.

3. All operators should be reinstructed on the operation of the mill feed system and instrumentation. Purging of the feed manometer lines by the operator should be reinstigated on a daily basis.

4. Change the material of construction of the manometer flexible leads to the mill from rubber to polyethylene.

5. With the system now in normal operation, the amount of time to actuate the protection system using a standard heat source should be determined. Crusting of resin compound on the alarm detection heads may be rendering the heads less sensitive to heat or light pressure.

6. Batch size of resin compound should be reduced to lessen the grinding time cycle.

7. All operations should be reinstructed on the handling, grinding, chemical and physical differences of one-stage versus two-stage resin compounds.

8. Modify the present CO_2 fire protection equipment with a dual release mechanism. This modification places the actuator lines and bulbs under slight pressure and will release CO_2 whenever the pressure increases or decreases.

CASE HISTORY NO. 964

Flammable Solvent Poured into Open Kettle

Description: An employee was pouring methanol into a five hundred gallon reaction kettle through an open manhole to neutralize the drying agent of a drying operation. As he was climbing down the stepladder to get more methanol, the vapors in the kettle ignited, blew out the manhole and hit him in the face. The employee received flash burns to his face and upper chest.

Causes: 1. Pouring flammable solvent into an open kettle with a possible ignition source.

Note: This procedure had been followed in small polyethylene jugs without incident. Adequate planning for transition to the larger vessel did not take place.

Preventive Measures: 1. The general procedure will be reviewed and revised.

2. All future neutralization will be carried out by pumping the methanol into a closed vessel with oxygen excluded.

CASE HISTORY NO. 965

Sprayed with Corrosive Liquid While Disconnecting Hose

Description: An operator was pumping DMF with with a portable pump from a 55 gallon drum into a stripper bottoms pump suction. Since the distance between the pumps was only three or four feet, the 50-foot rubber hose which was used was rather tightly coiled and apparently kinked. After pumping the contents of the drum, the operator closed the valves at the pumps and opened the bleeder to depressure the hose. After observing that the DMF had stopped draining from the bleeder, the operator then attempted to disconnect the hose from the stripper bottoms pump suction. As he did so, DMF sprayed from the connection onto his face, clothes and shoes. He immediately went to an eye bath located thirty feet away and washed out his eyes. He then returned to the control room, reported the incident to his supervisor, and went to the dispensary. He was then referred to a physician, and his eyes were found to be only irritated and no permanent damage was incurred.

Cause: The probable cause was that the hose was kinked and did not allow the pressure to be completely bled off prior to the hose being disconnected.

Preventive Measures: Metal "Flexitallic" hose with hammered type unions will be standard equipment in the ethylene plant for the portable transfer of all fluids except water. This replaces the common rubber hose and crows-foot connectors.

CASE HISTORY NO. 966

Mislocated Vents

Description: A man was overcome by methylene chloride solvent vapors mixed with inert gas, in a small infrequently used men's washroom located off an operating room floor. A five inch sampling-gauging pipe (covered with a metal plate) from a tank on the floor below terminated at the floor level in the washroom. A vent line from another system terminated just outside the window in the room. The employee has no clear recollection of events from approximately 9:00 a.m. until he was found by a mechanic at approximately 1:00 p.m.

Cause: Shortly after 9:00 a.m., the holding tank was drained. This could have permitted inert gas and solvent vapors to escape through the sampling-gauging pipe into the washroom. Later the tank was partially refilled which could also have forced vapors and inert gas out of this sampling-gauging line.

Investigation indicates that the window of the washroom was partly open during this same period and that subsequent to other events dope was pumped through the system to which the vent line was connected. It is conceivable that a slight westerly breeze could have forced the vapors into the room through the open window.

Preventive Measures: 1. The room will be eliminated so that it will become a part of the operating room where there is good ventilation.

2. Closures are being investigated for the sampling pipe opening to prevent the escape of vapors.

3. The vent terminating outside the window will be extended above the roof of the building.

4. Supervision in all departments are requested to conduct a search throughout their areas for connections or openings to tanks or pipelines which could be a hazard to people.

CASE HISTORY NO. 967

Unshielded Glass Acid Pipe

Description: An employee received burns on the face, arm and back when a 1 inch I.D. glass pipe containing sulfuric acid broke.

Two Field Department mechanics had completed repairs to a diaphragm valve located in a glass pipe line that was located overhead. They were wearing protective coats and overalls although they were not wearing head or face protection. When repairs to the valve were completed the injured employee was requested to check the operation of the valve to make sure it operated in a satisfactory manner. When this was done the two Field Department mechanics began replacing a large "L"shaped stainless steel guard over the glass pipe that protected it from physical damage. The two legs of the guard measured approximately 5 feet and 8 feet respectively.

Due to the unwieldiness of the guard the mechanics asked the injured employee to assist them in replacing it even though he was not wearing protective clothing. In their attempt to replace the guard the glass pipe was apparently struck. It broke off at a reducing nipple where it was connected to the valve.

One of the Field Department mechanics and the injured employee were splashed with approximately 1/2 gallon of concentrated sulfuric acid. The protective clothing saved the Field Department mechanic from injury, but the man from the operating department who was wearing only a skivvy shirt suffered the injuries noted above.

Although a safety shower and a hose were within 8 feet of the injured employee, he apparently became confused and ran approximately 80 feet from the scene of the injury to a location where he knew that a hose was available.

Preventive Measures: 1. No person should be allowed to work on or about the existing glass pipe without the guard in place unless the line is drained.

2. It is recommended that glass lined iron pipe be installed in place of the existing glass pipe.

3. All persons working on acid lines should be equipped with proper protective clothing designed to protect the head, eyes and body.

CASE HISTORY NO. 968

Protective Equipment Properly Used Could Have Prevented Injury

Description: The employee was standing on the lifting lug and chain guide at the end of a dempster tank. He had just removed the hose suction line from a 1-1/2 inch welded neck opening, and temporarily placed it across the tank vent pipe. This opening would not accommodate both a suction line and a measuring stick. He then used a steel rod to take a measurement of the liquid level. At this time the hose slipped over the vent pipe and the end flipped up towards the employee. Chemicals sprayed out of the open end of the hose onto the employee's face and the under side of his face shield which was in an off-the-face position. He received moderate burns to the face and a serious burn of the left eye.

Causes: 1. The presence of direct process residues that are very reactive with water.

2. The working area for the employee was not adequate due to a substandard dempster station.

3. The welded neck opening was too small to accommodate both a suction line and measuring stick.

4. The suction hose was placed in an insecure position across the tank vent line.

5. The employee was wearing his face shield in an off-the-face position.

Preventive Measures: 1. The Department will re-work the dempster station to conform to the Safety Standard. Specifically, the station will have a working platform that receives standard size tanks.

2. The Department having the waste chemicals will supply standard dempster containers or tanks acceptable to Waste Control.

3. The opening used for an adjustable dip pipe connection will be enlarged to accommodate both the dip stick and suction line.

4. The departmental safety rules and regulations will be reviewed with all plant personnel -- specifically, the necessity of having face shields in proper position while working.

CASE HISTORY NO. 969

Static Ignition of Sodium Hydride

Description: A hydrogen explosion occurred in a chemical process while solid sodium hydride was being charged to the still from a polyethylene bag. The still contained 750 pounds of reactant at 40°C. and 6-1/2 pounds of 50% oil-coated sodium hydride catalyst.

The normal procedure used on the previous fifteen runs was to charge the reactant under vacuum, break vacuum with nitrogen to a positive pressure and maintain a nitrogen bleed on the still while the manhole was open and at all times while processing also. Air had not entered the still for the past month.

In this instance, the operator (on this job only three days) attempted to pry open the manhole cover before the vacuum had been completely relieved and permitted air to be drawn into the still. He was immediately stopped and told to pressure the vessel with nitrogen before attempting to open the cover, and also told why this was necessary. After further pressuring with nitrogen, the operator opened the cover and a chemical engineer dumped the 6.5 pounds of sodium hydride into the vessel from a polyethylene bag. As the chemical engineer was shaking out the last of the hydride, an explosion occurred shooting flames into the air, knocking off his face shield, and driving him and the operator back from the kettle. The flames continued to issue from the kettle and the chemical engineer told the operator to close the cover to prevent the fire from striking back into the kettle. He turned up the nitrogen flow to the kettle. Flames continued to spurt several feet from the cover. By this time, two other technical men arrived with fire extinguishers and took over. They used dry powder extinguishers until the flames ceased and then opened the cover, replaced the gasket, bolted the cover down and applied vacuum. The batch was then processed in the normal fashion.

Cause: The three ingredients of explosion were present. The hydrogen from the reaction, the oxygen apparently from a pocket of air drawn in during the premature attempt to open the manhole, and the spark probably from a static charge on the polyethylene bag. The chemical engineer was wearing rubber gloves, shoe rubbers and dacron and wool clothing at the time.

Preventive Measures: The succeeding batches were run with sodium methylate as a catalyst replacing the sodium hydride. However, if it becomes desirable to use hydride again, several changes may be made. First, the sodium hydride will be handled in static-proof bags. Second, the order of adding first and third constituents was reversed as catalyst does not react with third unless first is present. Vessel is then closed after adding catalyst (second constituent) and the reactive constituent (originally first) is drawn into the closed still by evacuating it. This change may have some effect on product quality which will have to be investigated.

CASE HISTORY NO. 970

Metal Float Ruptures under Pressure

Description: A large stainless steel float about 2 feet in diameter had been fabricated according to our specifications by an outside concern. The pipefitters were given the job of testing it for leaks since it had several welded seams. They had been instructed by their foreman to put about 5 lbs. of air on the float and then paint the welds with soap suds to determine if there were any leaks. The foreman suggested that the air hose be attached to a nipple without any pipe clamp so that it could blow off in case of an emergency. A short time later as the pipefitters were carrying out their tests, the float ruptured violently. Fortunately there was no fragmentation of the metal and no personal injuries.

Investigation showed that one of the pipefitters had gone to the instrument ship and requested an accurate gauge since they wanted to put no more than 5 lbs. of pressure on the float. The instrument man was quite busy at the time and handed the pipefitter a new gauge which he had hanging on the wall. This turned out to be a vacuum gauge and was calibrated at 0-30 inches of mercury. Unfortunately the markings indicating that it was a vacuum gauge were in very small letters close to the full scale deflection and were not easily discernible. In addition, the pipefitter had applied a clamp to the hose at the nipple so that the pressure could not be readily relieved in that area. A hydraulic test would have probably been more appropriate for this type of equipment, but this was not very feasible since there was only one opening in the float.

Cause: A closed system should never be pressure tested without some sort of pressure relief device to prevent exceeding the designed pressure. The system was not equipped with such protection and this was the main cause of the accident.

The air line in question carried 100 psi and a regulator in the line which stepped the pressure down to 5 lbs. would probably have prevented an injury, but such was not used.

A vacuum gauge instead of a pressure gauge was installed on the float because of the difficulty in distinguishing one from the other.

Preventive Measures: In the future, a proper gauge, a regulator, and suitable pressure relieving device will be used for pressure testing with air or any other gas.

CASE HISTORY NO. 971

Mixing of Chemicals-- Hazard Unrecognized

Description: An employee was attempting to mix liquid chlorine and carbon bisulfide for use with infrared equipment to determine chlorine impurities. The equipment in use consisted of one cylinder containing liquid chlorine (30 cu. ft. size), one 1700 ML metal pressure cylinder (400 psi test) containing 70 ML of carbon bisulfide and 1/4 inch copper tubing with fittings to connect the two cylinders. The equipment was assembled in a ventilated lab hood. In addition, a portable 3/8 inch plastic shield with a lead base had been positioned in front of the equipment as splash protection against any liquid chlorine spill. An explosion occurred inside the 1700 ML cylinder as liquid chlorine was introduced. The employee received cuts across the back of his left hand and a possible broken bone in his hand near the index finger.

Cause: Employee failed to recognize the potential hazard of mixing liquid chlorine and carbon bisulfide in the presence of an iron catalyst (1700 ML cylinder).

Note: The operation had previously been performed using glass-lined containers.

Preventive Measures:

1. Check lists and available technical data should be consulted before attempting experiments and/or routine lab operations.
2. The necessity of considering all safety aspects involved before proceeding with any operation will be stressed.

CASE HISTORY NO. 972

Sulfuric Acid--Loss of Sight

Description: A powerhouse employee pumped about 500 ccs. of sulfuric acid from a carboy into a ceramic pitcher. With the pitcher in his hand, he walked toward the welder water cooling tank, located about 15 feet away from where he obtained the acid. In doing so, he tripped over a drainpipe which ran across the floor near the steps leading to the tank platform. As he fell against these steps, his face shield was tossed from his head and some of the sulfuric acid splashed against the left side of his face and into his left eye.

He went immediately to an emergency shower about 15 feet away and washed the acid from his face. After receiving first aid treatment in the plant medical department, he was removed to a local hospital. The eye was treated for several days and it appeared to be making satisfactory progress. In fact, he was able to return to work about a week after the accident. However, approximately two weeks later, complications developed and the eye had to be removed surgically.

Preventive Measures: The drainpipe has been removed, eliminating the tripping hazard, and the ceramic pitcher has been replaced with a plastic container which can be closed completely.

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 973

Inert Gas Leak in Pit Claims Life-- Quick Action Saves Another

Description: A contractor employee (apprentice pipefitter) was asphyxiated when he entered a pit, apparently to check for an inert gas leak from piping in the valve pit.

The welding on a piping system in underground tunnels and pits was being tested for possible leaks by using compressed nitrogen. After the nitrogen supply was exhausted, cylinders of argon gas, which were available close at hand, were used to continue pressurizing the piping during the test. Since the piping would not hold pressure, more gas was needed and the apprentice was sent by the pipefitter to arrange for additional cylinders of gas. Shortly thereafter, the pipefitter was walking to the pipe shop by way of the valve pit and, as he glanced into it, he saw the apprentice lying in the pit bent backward over the pipe. Another pipefitter, hearing the first shout for help, ran to the pit and started squeezing into the restricted hatch opening. At the same time, an engineer directed someone else to call the ambulance and then went to the pit. Another man ordered the air compressor started and a hose from it was handed to the engineer. In the meantime, another man was sent to cut the remaining gas pressure on the pipeline.

The engineer then observed that the pipefitter who had entered the pit had also collapsed. He then directed the airstream from the hose into the pit and then, with the airstream blowing across his own face, climbed down into the pit. While he was lifting the two unconscious men into upright positions, other men were ripping and sawing the form lumber from the hatch opening to provide more space for removel of the men. With this done, the pipefitter and the apprentice were lifted from the pit in that order.

Mouth-to-mouth resuscitation was immediately given to both men. One or two minutes later, medical assistance arrived. By this time, the pipefitter was breathing unassisted. A doctor immediately took charge of the resuscitation effort on the still unconscious apprentice but subsequently pronounced him dead.

Preventive Measures: There are many safety standards and procedures that have been published outlining safe practices for entering and/or working in pits, tanks, etc., where there may be a deficiency of oxygen and/or the presence of toxic of flammable gases. Most such standards or procedures caution: Never enter small confined spaces until the atmosphere has been checked with reliable instruments or until adequate forced ventilation has been provided to remove contaminated air and assure an oxygen-efficient atmosphere or until men are equipped with the proper type of self-contained breathing equipment, safety belts or harnesses, and life-lines and attendants. (See MCA Safety Guide SG-10, "Entering Tanks and Other Enclosed Spaces".)

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 974

Autoclave--Hot Water Release

Description: A thermal burn resulted in lost time when an abnormal amount of hot water flowed out of an autoclave door. The operator started the autoclave sterilization and left for lunch. When he returned he observed that the sterilization temperature had not been reached. The operator shut off the steam, vented the autoclave and opened the by-pass valve on the steam trap. After the pressure was vented he opened the door. An unexpectedly large amount of hot water flowed out and came in contact with his feet causing second degree burns.

Cause: Drain lines to the steam trap were examined and found to be free of blockage. An examination of the interior revealed the presence of one piece seals at the far end of the autoclave. It is assumed that a vial seal plugged the drain opening and prevented the steam condensate from escaping.

Preventive Measures: To prevent a recurrence the following has been done:

1. Re-instruct operators to check the autoclave prior to loading to make certain there is nothing to cause the drain line to become plugged.
2. A perforated standpipe has been installed in the drain opening.
3. Piping changes now permit the operator to check for the presence of condensate before opening the door.

CASE HISTORY NO. 975

Self-contained Breathing Apparatus Proves Inadequate

Description: The demand for breathing-air exceeded supply in cylinder and resulted in chemical exposure. A supervisor noticed acid fumes in the area of an outdoor storage tank containing dilute Ethanolic HCl. He donned a five minute self-contained breathing apparatus and upon investigation determined that the material was flowing onto the ground from the broken glass bottom outlet line. The air supply became depleted and he inhaled some of the fumes. He obtained a larger unit and succeeded in closing the bottom valve with a wrench.

He felt dizzy and reported to Plant Health along with two operators who were exposed to the fumes. No one was seriously injured but several lessons can be learned from this incident.

Cause: The glass line was rigidly fastened to the pump and probably broke due to stresses transmitted by the corrosion of the pump fittings.

Preventive Measures:

1. An armored Pyrex expansion joint in the line would have reduced leakage.
2. Operating personnel have been instructed that all vessel bottom outlet valves must remain closed when not in use.
3. Five minute air cylinders are acceptable for quick rescue work. Larger sized cylinders with low pressure alarms should be available for all other emergencies.

CASE HISTORY NO. 976

Silver Complex Detonation

Description: Recently an employee received chemical burns to both eyes when the reaction he was conducting detonated, throwing a silver ammoniacal complex over the laboratory.

The employee was not wearing safety glasses even though they were provided.

The reaction he was conducting was to prepare a silver ammoniacal complex as a part of his research assignment.

He had added sodium hydroxide to a silver nitrate water mixture until the silver nitrate had precipitated as silver oxide, then he proceeded to add ammonium hydroxide. While adding the ammonium hydroxide the reaction heated, and a detonation occurred.

Literature references on this reaction state that the reaction of ammonium hydroxide on silver oxide can cause the formation of fulminate of silver and the records show frequent detonations.

The employee should have used the established alternative method which requires the addition of ammonium hydroxide to the silver nitrate water solution which can be performed with safety.

Preventive Measures:

1. Safety glasses must be worn by everyone in all chemical laboratories.
2. New employees should be advised of hazards which might be encountered in their work.

CASE HISTORY NO. 977

Pressure Release from Disused Line

Description: Eruption from a sulfuric acid line did not cause serious injury but revealed a dangerous condition. About 75 feet of 1-1/2 inch carbon steel line ran from a second floor concentrated sulfuric acid tank to a first floor receiver. The valve below the acid tank and the valve in the line above the receiver were both closed for about a month. When an operator opened the valve at the receiver, pressure in the line blew out a gasket on a porcelain section between the receiver and the valve on the carbon steel line. The acid and precipitated ferric sulfate, which evidently plugged the one inch nozzle into the receiver, sprayed out over a wide area and on to the operator. The injured man quickly got under a shower and removed his clothes. He received a second degree burn on his left forearm. His clothes were literally destroyed.

Cause: This is a graphic illustration of what can happen when a section of pipe containing a corrosive material is isolated. The hydrogen generated by the action of the acid on the steel must have developed high pressures.

Preventive Measures: To prevent a recurrence, all areas in the plant will survey their sulfuric acid systems for seldom used or abandoned lines and take proper steps to prevent this type of occurrence. Dry vents will be installed on sulfuric acid tanks to prevent introducing moisture into storage tanks, which accelerates pipe corrosion.

Mechanically interlocked cocks to drain and vent seldom used lines containing corrosives should be considered.

CASE HISTORY NO. 978

Unloading Ammonia Tank Car

Description: After loading another tank car, an employee passed by the compressor being used to unload an ammonia tank car and noticed a pressure reading of 190 lbs. He concluded that the excess-flow check valves in the tank car liquid unloading line were closed and followed the accepted practice in this situation of stopping the compressor. He then went to the top of the tank car to close the valves in the tank car liquid unloading line. He closed one, leaned over the relief valve to reach the other and had it almost closed when the relief valve (set at 225 lbs.) opened. Later it was indicated the valve opened at 210 lbs. The "blow" lasted only five to eight seconds but discharged ammonia vapor into his face and into his mouth. Chemical goggles undoubtedly saved his eyes from injury.

Cause: Failure of supervision to establish safe operating procedures.

Preventive Measures: Operating procedures have been changed to install valves at platform level and close these before closing those on top of the tank. In addition, a breathing-air system will be installed for the employees' use during the short time nearness to the tank car relief valve is necessary.

CASE HISTORY NO. 979

Hydrogen Peroxide Splashes into Eyes

Description: An employee had disconnected the pipe between the 70% hydrogen peroxide pump and the tank trailer filling station at bulk terminal in preparation for hooking up and unloading a tank trailer due to arrive. The line was broken above a closed valve at the discharge of the pump but was not locked out. Because some hydrogen peroxide was running down over the pump, the employee opened the valve, inserted a water hose, and washed out the discharge side of the pump. He failed to close the valve. When it was decided about two hours later to reconnect the broken line to load a tank trailer, the employee stood on the dike wall and was in the process of lining up a pipe flange, gasket, and valve flange above the pump when his foot struck the butterfly switch, starting the pump and discharging the pump's contents into his face with such force and at such an angle as to dislodge his goggles. Hydrogen peroxide splashed under his goggles and into his eyes. Fortunately, he was able to prevent very serious burns by immediately washing his eyes for fifteen minutes under a nearby shower and then for five minutes with a water hose.

Cause: Failure to de-energize pump.

Preventive Measures: Additional training is planned and the importance of strict adherence to lock-out and tagging procedures is being re-emphasized.

4. Continued emphasis on indoctrinating employees to be more aware of hazardous conditions and operations.

CASE HISTORY NO. 980

Improper Use of Hand Tools

Description: While transferring a batch of polymer from a kettle to a blow-down tank, the discharge line became plugged. The employee turned off the agitator to see if his attempt to unplug the line had been successful. The agitator was coasting, and the employee put an 18-inch pipe wrench on the stub shaft to stop the rotation by letting the wrench handle strike against the agitator motor support. The employee's left index finger was pinched between the wrench handle and the "A" frame support. The incident resulted in amputation of the left index finger at the first joint.

Cause:
1. The valve on the discharge line plugged.
2. The agitator coasts for approximately thirty-five seconds after being turned off.
3. The employee deviated from operating instructions.
4. Impatience because of plugged valve.
5. Using pipe wrench on stub shaft to stop revolving agitator.

Preventive Measures:
1. Instructions against using tools on this type of moving equipment will be written into safety considerations for this job.
2. Determine feasibility of installing high pressure water jets in kettles to reduce polymer build up during a reaction.
3. Polymer build up will be more critically assessed to determine when build up is great enough to cause chunks to break off that might plug the valve.

CASE HISTORY NO. 981

Operator's Arm Caught in Large Ribbon Blender

Description: A Chemical Operator caught his right arm between the spiral ribbon and shell of a 191 cubic foot double spiral Ribbon Blender.

The operator was assigned to brush down the Dust Collector and Ribbon Blender from the outside for a routine product change over. The Blender is located on the second floor over the packaging station. Without telling his supervisor, and without requesting a lock-out of equipment (per standard procedure), the operator removed the blender cover and entered the blender to brush the unit down. The packaging operator on the first floor not knowing what the other operator was doing, turned on the blender to package the last of the material in the blender that had accumulated from the Dust Collector clean-out. The operator in the blender called "Hey" twice. The department head who had entered the packaging room heard the "Heys" and turned the blender off immediately. The blender was running approximately 5 seconds, or enough time to make one revolution. The department head ran upstairs and found the operator's upper arm pinned between the spiral ribbon and the blender wall. Aid was immediately summoned and the spiral ribbon was cut out with hacksaws and the operator removed to the hospital by the ambulance squad. The operator suffered multiple breaks, lacerations and contusions of the right arm only. He is now undergoing medical treatment.

Cause: The operator should not have entered the blender without following the standard lock-out procedure for these blenders. This means having the supervisor, in the man's presence, lock-out the main switch in the electrical panel room and give the key to the operator who only then can enter the blender.

Preventive Measures:
1. A written procedure covering the lock-out procedure is being prepared and will be the subject of the next Department Safety Meeting.
2. Electrical interlocks will be installed on the blender covers, so the blender cannot be operated with the covers removed.
3. Whenever the equipment is brushed down from the outside, the lock-out procedure must be followed.

4. This accident has been covered in detail at the monthly Plant Safety Meeting.

CASE HISTORY NO. 982

Splashed with Sulfuric Acid--Sample Point Unauthorized

Description: The circumstances leading up to the injury were as follows: Normal procedures call for drawing a sulfuric acid sample every two hours from a sample point at the suction lines (5 psi) of the P-5 pumps to test the strength of the acid to the HCL drying column. These sample points were not enclosed in sample boxes. On June 30 pump No. P-5A developed a leak around the packing and since it was felt unsafe to pull up further on the packing, pump No. P-5 was put in service at noon. The injured operator reported to the supervisor soon afterward that the valve on the sample point at P-5 was very difficult to open and close and he was unable to use it for taking his samples. The supervisor informed him that the next day, July 1, they would put P-5A in service long enough to replace the faulty valve on P-5. For the remainder of that day the subject drew his sample from a 1/2 inch bleed valve on the discharge line (50 psi) of the pump downstream of the acid cooler. Other extenuating circumstances were that the suction valve on P-5A (bad packing) leaked through to such an extent that it could not be isolated and repaired until the drying system was shut down and drained.

At 11:00 a.m. on July 1, the injured employee prepared to draw the sulfuric sample, and rather than use the 1/2 inch bleed valve downstream of the acid cooler he had used previously, looked about and decided to use a new recently installed 1 inch block valve on the suction line to the pump near the drying column. This line is approximately 6 ft., 6 in. above grade with the discharge of the valve at or near face height, depending on the height of the individual. This was not and had not been a sample point, but was in the line for draining purpose. The shift supervisor was unaware of the operator's intent to use this valve, and the operator was unsure why he chose this spot for sampling rather than use the one at the cooler. Prior to his attempt to take the sample, he had placed the graduate below the drain valve and was cautiously opening the valve when he was splashed and sprayed with acid about the face, neck, chest, and arms. The supervisor later discovered material in the graduate that indicated saddles from the tower had evidently plugged the valve and when the valve had been opened far enough, had broken loose with a gush, struck the bottom of the graduate, and deflected back onto the injured's face and upper body.

After the accident, the subject was able to make it to the safety shower approximately 10 feet away and with the immediate assistance of an operator who happened to be nearby, started to flush the affected area with water. The supervisor and operator displayed excellent judgment and kept the injured man under the shower for 15-20 minutes after which he was taken to the hospital, by ambulance, for medical attention. The employee sustained 2nd degree and possible 3rd degree burns to the lower face and neck with 1st and possible 2nd degree burns to upper chest and right arm. Chemical goggles unquestionably saved the man from very serious injury or loss of both eyes.

Cause: Investigation determined the accident causes to be:

1. Use of improper sample point at an unsafe location. Corrosive sample should never be drawn above waist height.
2. Plugged valve.
3. Poor judgment in opening valve above safe limits due to plugging.
4. Inadequate protective equipment for hazard involved.

Preventive Measures: The following recommendations for corrective action were agreed upon by the Investigation Committee:

1. That a permanent order be issued for sampling corrosive materials, with sample stations conforming to a uniform specification throughout the plant.
   a. Sample stations be provided with a minimum 1 inch line and valve back welded or flanged.
   b. All sample lines have double block valves installed.
   c. Sample lines be enclosed in lead box with observation window on one side.
   d. Sample boxes installed below waist height and stations clearly marked.
   e. Sample points be inspected weekly for corrosion or cracks.
   f. Sample will not be taken at any location other than designated location without the approval and direct observation of the supervisor.
   g. Acid hood, rubber coat, and rubber gloves be required for normal sampling.
   h. Acid hood, rubber coat, pants, gloves, and boots will be required for sample at any location other than normal sample point and when depressuring or bleeding equipment in corrosive service.
2. Plugged lines, proper procedure for opening valves, and the associated hazards will

be discussed with the man when he returns to work.

3. The faulty sample valve on the P-5 suction line has been repaired.

CASE HISTORY NO. 983

Chemical Spray

Description: This accident occurred in the salt removal portion of the hydrazine production plant. The specific equipment involved was an 8-inch sight glass in the line from the slurry thickener to the mother liquor tank. There had been repeated instances of the 8-inch Pyrex view plate cracking due to the difficulty in adjusting the four bolts on the glass support ring. There was also a tendency for the highly alkaline mother liquor to etch the back of the glass making viewing difficult. Approximately 45 days before the accident, a piece of 1/4-inch Plexiglass was substituted for the 3/4-inch eight-inch diameter Pyrex glass. It was found that the plastic would not crack and was not affected chemically by the solution. Since this system normally operates under little or no pressure at this point, it was felt that the substitution was justified. On the day of the accident, the line below the sight glass became filled with liquor and the overflow from the thickener was stopped. The employee, believing that the line was under vacuum rather than pressure, attempted to vent the line by loosening the two top bolts of the sight glass support ring. As soon as the ring was loosened, the plastic which heated beyond its softening point, pulled from beneath the flange and then broke. The hot liquor sprayed forcefully onto the employee's face and body, resulting in first, second, and third degree burns to approximately 20% of body surface including face, and burns to cornea of both eyes.

Cause: Three basic things were involved which contributed to or caused this accident.

1. Use of material in the salt removal system which could not tolerate the 255°F liquor temperature.

2. Unsafe act on the part of the experienced foreman in making an adjustment to a process line while in operation.

3. The flaw in the process which would allow a portion of the system which would normally be at atmospheric pressure to become pressurized to an estimated 30 to 35 psig.

Preventive Measures:

1. In order to eliminate the problem of vapor lock in this mother liquor line, a condenser had already been ordered and was due for delivery 5 days after the accident occurred. This unit will be installed and will eliminate such difficulty in the future.

2. The sight glass will be modified to reduce the view port to 5 inches which should eliminate the breaking problem experienced in the past. It is possible that a thick Plexiglass plate will be used if tests indicate it can survive the designed capacity of the sight glass unit.

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 984

Hose Failure--Sulfuric Acid Burns

Description: The shift foreman and the injured employee attempted to fill two containers with sulfuric acid drawn from a filter drain in a chlorine dioxide plant. The sulfuric acid was needed for a water treatment plant because the steam and recovery unit was inoperative.

When the drain was opened, the rubber hose ruptured. The injured was sprayed with sulfuric acid, suffering burns of the face and neck. Safety glasses protected his eyes.

Cause: Action of the acid on the lining of the rubber hose caused the hose to collapse and form a blockage. When pressure was applied the hose ruptured at the point of blockage.

Preventive Measures: The hose was removed and replaced with a permanent drain line to the sewer. All workers have again been instructed to wear proper protective clothing when handling or working with acids. This will include full face shield, rubber gloves and rubber clothing.

CASE HISTORY NO. 985

Removal of Safety Seal Assembly from Active Vessel under Heat and Vacuum

Description: A pipefitter assigned to the process expansion was instructed and shown by the area production supervisor and the group leader to remove a safety disc from the deactivated No. 1 still. This disc was to be used on a new vessel being installed. Approximately 6:00 p.m., the pipefitter and group leader asked the process foreman if they could remove the designated disc. Permission was given, but it was not until 8:30 p.m. that the pipefitter, thinking he was working on the No. 1 still as previously shown, actually removed the safety seal assembly from the adjacent active No. 2 still. A blank was substituted but not securely bolted down. Fortunately, at the time, Still No. 2 was in the process of cooling prior to dropping the residue. At approximately 4:00 a.m. the next morning, an operator noticed that the safety disc had been removed when, upon purging the vessel with CO_2 prior to dropping the residue, fumes emitted from the loosely connected blank. Several hazardous conditions could have resulted if the No. 2 still was not in the cooling phase, such as: formation of hazardous decomposition products which are potentially explosive upon contact with air; building could have filled with flammable and explosive vapors; pipefitter could have been hit with hot vapors if No. 2 still was in stripping phase; sudden break of vacuum could have caused residue to erupt and spill out through pipe if source of heat was not turned off.

Preventive Measures:

1. Tag all vessels or parts of vessels that are scheduled to be worked on.
2. Identify all vessels clearly.
3. All maintenance foremen should be advised of the potential hazards in every process.

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 986

Ethyl Acetate Tank Truck Explosion: Static Electricity

Description: At about 1:45 P.M., a tank truck being loaded with 99% ethyl acetate, exploded. The tank truck loader had started to load the truck at approximately 1:41 P.M. Just before the explosion occurred, the loader heard what he described as a sizzling sound as from a frying pan. He peered into the tank but could see nothing. He moved away but held an arm over the dome opening holding a wooden gauge stick. An explosion occurred and flames shot out of the dome opening. The loader's right arm and hand received second degree burns. He jumped from the top of the truck to the ground. Torn ankle ligaments and inner thigh muscle strain resulted.

Investigation at the scene of the accident showed all grounding equipment to be in excellent condition. The hose used in loading was checked and found to have a resistance of less than 50 ohms from end to end. Questioning of personnel disclosed that regular grounding procedure had been followed by the tank truck loader. However, it was disclosed that static discharge had been heard before but not recognized as such. Static discharge had been seen jumping between the copper cup used to hold the thermometer and the loading pipe, at the start of loading. In all cases, 99% ethyl acetate had been involved. Practice of lowering the thermometer into the truck had been discontinued at the time the discharge was seen.

Cause: All evidence shows this explosion to have been due to free charge on the surface of the liquid. Discharge of sufficient energy resulted in ignition of flammable misture.

Preventive Measures:

1. The pumping rate is to be slowed down so as to decrease turbulence and thereby cut down static build-up.
2. Bare No. 4 flexible stranded copper cable is to be used on the outside of the cloth filter to discharge static. Six to eight cables shall run from upper two inch fitting to lower two inch cap and extend six inches beyond bottom fitting.
3. No ungrounded metal objects are to be inserted into tank truck during loading operations.
4. After loading has been completed, a three to five minute relaxation time shall be allowed before proceeding with taking of readings. Relaxation time should allow dissipation of any static charge.

CASE HISTORY NO. 987

Explosion and Fire--Lead Azide

Description: At approximately 8:35 A.M. an explosion and fire occurred in a lead azide conditioning and storage magazine which resulted in the death of a chemical worker. The building was demolished. The chemical worker and his co-worker were checking magazine bunkers to determine if heating systems were functioning satisfactorily, at the time the explosion occurred. Both men proceeded separately, with the chemical worker checking the lower level of buildings (which included the building in which the explosion occurred). His co-worker completed a check of a similar set of buildings and was waiting for the chemical worker at the time of the explosion. Two explosions were heard, one immediately followed by another louder report. The building was 8 ft. 2-1/2 in. x 13 ft.-3/12 in., with 10 ft. ceiling and a 3 ft. 6 in. addition to the northeast corner for housing the steam reduction unit. The building was of semipermanent type construction with concrete foundations and floors. It was not sprinklered or fire resistant. The exterior walls were of corrugated asbestos siding over a wood frame. The roof was of tar and gravel built up over wood decking. All interior walls and ceiling were of fiberboard. The building had a conductive floor, static electric grounding facilities, and steam and electric utility connections. Lighting was accomplished by a spark proof light mounted in the wall over the door. A ventilator was installed in the roof. The door was equipped with ground cables attached to the building ground system. A static discharge bar was installed just inside to the left of the door. Two inch blanket insulation covered with aluminum foil vapor barrier was installed in the walls and ceiling. The hot water heating system and humidification control system located in the building were demolished, with the exception of the fin-type hot water radiators which remained largely intact. Other equipment in the building consisted only of a small metal table and metal shelves, all of which were completely demolished. A total of 20 pounds of lead azide was located in the building - 15 pounds in conductive rubber drying tubes and 5 pounds in pie cups. Interior temperature of the building was approximately 80°F, with relative humidity less than 10%. An inspection conducted approximately 3 months prior to date of the incident found all equipment to be properly grounded. The barricades effectively contained the explosion and were damaged only as a result of the fire. The barricade's wooden retaining wall was ignited along the top edges and fire spread down the wooden retaining walls before being extinguished. Debris was blown to a distance of approximately 400 feet, with most of the debris (including wood and corrugated transite) confined within a distance of approximately 140 feet from the point of explosion.

Cause:

1. Accumulated static electricity discharged from the body of the deceased to the lead azide, causing the explosion. (The deceased was wearing non-conductive rubber overshoes over conductive shoes.)

2. Lack of adequate supervision, through a system of positive controls, definitive instructions, and approved SOP's, allowed violations of safety regulations to exist and was a contributing factor to the explosion.

3. Condition of walkways leading to the building, which were not cleared of snow and which contained loose gravel, may have been a contributing factor to the explosion.

Preventive Measures:

1. The practice of wearing non-conductive footwear in and around buildings containing explosives be discontinued immediately.

2. A positive system of safety checks by supervision be established, to insure that employees are properly attired and equipped when entering explosive areas, and that these safety checks be made a matter of record.

3. Approved SOP's be established for all plases of explosive material processes, to include monitoring and conditioning operations.

4. Walkways in areas containing explosives be conditioned to eliminate the presence of loose abrasive materials, and be kept clear of any hazards such as ice, snow, or water.

Armed Services Explosives Safety Board Case History

CASE HISTORY NO. 988

Tank Explosion

Description: An explosion and fire occurred at a research combustion and heat transfer laboratory, resulting in fatal injuries to an engineering test technician. Preparations were being made to test an oxygen propane torch intended for later use in the evaluation of flame resistant materials. Liquid oxygen at a pressure of 200 psig was to be run through a throttle valve and heat exchanger to furnish gaseous oxygen to this torch. The set-up utilized a nitrogen gas pressurized liquid oxygen tank facility constructed some two years ago for heat transfer testing, but which was not so used. The system had been secured against contamination during the idle period. On the day prior to the accident, the oxygen system was checked out with liquid nitrogen and the throttle valve was adjusted to give the proper flow rate to the torch. On the day of the accident, the propane system was flow checked and adjusted to flow rate. Then the LOX system was loaded, and at the time of the accident, nitrogen pressurization of the tank was in process. The crew was increasing nitrogen gas pressure in the tank in small increments to the intended level of 200 psig. The technician was viewing a tank pressure gauge from a distance of about 10 feet and had just called out "150 psig" when the explosion and fire occurred. Positive evidence showed that the system was mechanically sound and that the tank was not over-pressurized with nitrogen. The deliberation and care with which the pressurizing operation was proceeding indicates that the nitrogen pressurization was only slightly above 150 psig. The tank was protected with a relief valve and burst diaphragm set to 1200 psig. After the incident, a loosely fitted dust cap in the relief valve discharge port was still in place, indicating that the valve had not opened. Subsequent testing of the valve showed it to be still in good condition and operating properly at its setting of 1150 psig. The burst diaphragm also was tested and burst at 1200 psig.

Cause: Probable cause of the explosion was the sudden generation of pressure due to reaction of the liquid oxygen in the tank with the material of the tank. This tank was made of titanium alloy. Examination of the debris showed extensive burning of the lower half of the tank; some fragments burned to a feather edge, and a portion of the tank bottom was apparently completely consumed by fire.

Comments: Literature search has not revealed any definite prohibition against the use of titanium for oxygen services; however, several references question such use and indicate that titanium is more sensitive to reaction with oxygen than with other common materials of construction, such as stainless steel or aluminum. Oxygen/titanium reactions have been noted on a number of occasions, usually as a result of some triggering action. It was assumed the tank was suitable for liquid oxygen service because the specification under which it was purchased called for pressure cycle testing at -320°F and to 5000 psig pressure, a value several times the pressure at which the tank was to be used. It had been given a pressure test at 4500 psig and cleaned for LOX service just prior to incorporation in the facility. Contamination of the system may have been a factor in the triggering of the reaction between LOX and titanium because most such reactions noted have been the result of some triggering action. Careful analysis of the components of the pressurizing system, the tank remains, the downstream LOX flow system, the liquid nitrogen supply tank, the liquid oxygen supply tank, and the transfer hose do not show presence of contamination. Whether or not contamination played a role in the accident is unknown.

Preventive Measures:

1. Eliminate use of titanium in service with oxygen – liquid or gaseous.
2. Additional chemical and metallurgical tests are proceeding on the tank and certain of the LOX flow system components.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 989

Using Steam to Unplug Tar Line

Description: Employee was preparing to discharge the contents of a tar receiver to a dumpster box. He opened the outlet valve on the receiver and observing the product would not flow out, applied steam through a permanent connection to the outlet line. Immediately after turning on the steam, the plugged line cleared and the operator turned off the steam. However, the initial surge of steam into the receiver caused the hot tar to spray out of the vent and the porthole on top of the receiver, spraying the employee.

Cause: The receiver porthole cover, which had been removed to repair a high-level alarm, had not been bolted down securely. Also, the receiver had been filled with more product than usual to check the functioning of the high-level indicator. The steam pressure caused the hot tar to surge out of the receiver through the open vent and loose porthole cover.

Preventive Measures:

1. The vent discharge will be shielded so as to confine any spray. The porthole cover will be bolted tightly before steam is applied to the outlet of the tar tank.
2. A flush valve will be installed on the outlet of the receiver to minimize formation of plugs.
3. An extension handle will be provided so that the steam valve can be turned off at a safe distance from the receiver.
4. The possibility of eliminating the tar receiver by providing a direct discharge of tar to a ventilated dumpster will be investigated.
5. The accident will be reviewed with all supervisory and operating personnel to emphasize the hazards inherent in the use of steam or air pressure to unplug lines and valves.

CASE HISTORY NO. 990

Oil Bath Sprays Employee

Description: The injured employee was preparing an epoxy material for analysis of its molecular weight. A cold finger condenser was fitted to the test tube which contained the sample dissolved in pyridine. Pressure developed in the test tube as it was heated in a glycol bath. The test tube broke as it was forced against the bottom of the bath. The pyridine vaporized causing the glycol to spray out of the bath and onto the employee's face and hands. Moderate thermal burns to the face, neck, forearms, and hands were sustained by the employee.

Cause:

1. Pressure built up in the test tube because heat was applied to a closed system.

2. The setup was not vented.

3. The heating bath was not controlled nor did it have a heat measuring device.

Preventive Measures: 1. All laboratory setups will be provided with an adequate vent to prevent pressure build up.

2. Laboratory setups will be checked over by a second person.

3. The hazards of oil baths will be discussed in area safety meetings.

CASE HISTORY NO. 991

Unsafe Loading of Pallet

Description: A serious injury could have resulted when an employee, in handling a 55 gallon drum of oil weighing approximately 350 pounds, fell from a building loading dock onto a load lugger bucket. The drum, in falling with him, pinned the employee to the edge of the opening to the load lugger bucket and the building dock.

A fork truck operator had lifted a pallet with a fork truck to the level of the building dock for loading a 55 gallon drum of oil. He then went into the building to get a drum truck for moving the drum onto the pallet. The employee, wishing to help the operator, elected to move the drum from the dock onto the pallet by rolling it on the chime. While rolling it onto the pallet, the employee's foot slipped causing him to fall into the opening made by the raised pallet, building dock and a load lugger bucket. He landed on his back across the bottom edge of the opening to the bucket with his left foot up on the dock. The drum of oil tipped over, pinning the employee between the load lugger bucket and the dock. The bottom edge of the drum was resting on the pallet. Employee received a bruise across his back from the edge of the load lugger bucket.

Preventive Measures: 1. The 55 gallon drum of oil should have been handled with the use of a drum truck designed for loading and unloading pallets.

2. The pallet should have been placed on the platform for safer loading of drums of material.

CASE HISTORY NO. 992

Fire During Waste Disposal Operations

Description: A 250-pound metal drum of waste ammonium perchlorate was delivered to the burning ground in a 1/2-ton pickup truck for disposal. The material had been rejected due to the top section of the drum rusting, allowing the material to cake from moisture. The truck was parked alongside a designated pit which contained a quantity of dry solid propellant trimmings and approximately 300 pounds of wet propellant waste. Two employees tossed the drum over the side of the truck bed and allowed it to fall into the pit, a height of approximately 9 feet. When the drum contacted the bottom of the pit, ignition of the propellant trimmings occurred. The two employees evacuated the area, receiving only minor burns from the radiant heat.

Cause: The most probable cause is impact of the propellant trimmings between the ammonium perchlorate drum and rocks or other objects in the pit bed.

Preventive Measures: More rigid handling and disposal procedures have been implemented and are being enforced.

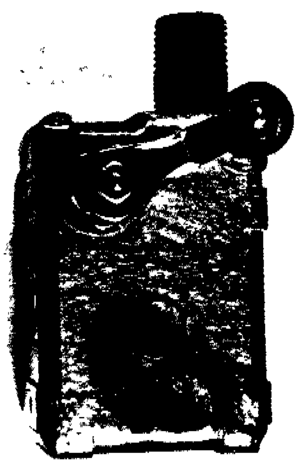
Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 993

Microswitch Failure--Fire

Description: During the centrifugation of a water base compound, an operator observed flames erupting from an electrical switch on the cover of a centrifuge and also in an open trash can containing paper, mill-ends and spent carbon, located 15 feet away. The operator quickly extinguished the fires by using a CO_2 extinguisher.

Investigation on the scene revealed that the switch burned through its aluminum explosion-proof case. The heat and pressure ruptured the case and propelled a piece of molten metal into the trash can. The illustration shows the rear of the case where the failure occurred.



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Cause: A complete investigation revealed that this control switch was subject to a high intensity arc due to a short circuit in the system. Although the switch is designed for 440 volts, it is rated for a maximum of 15 amperes. When the short occurred, it was subject to the full 60 ampere load.

Preventive Measures:

1. An Engineering Standard has been revised to show how all control devices on 440 volt circuits will be fused separately in the motor starter box with a three ampere fuse.

2. All new installations should be made so that each member of each circuit is protected properly against overload. Existing installations should be reviewed and corrections made in critical areas where necessary.

CASE HISTORY NO. 994

High Temperature Reaction Out of Control

Description: While charging the acid in a typical "alkyd" resin reaction (alcohol and acid), part of the solid acid charge hung up in the weigh tank above the reactor. With the catalyst already added, the delay in completing the charging failed to cool the batch sufficiently below reaction temperature and a violent reaction occurred, sending a flammable by-product gas out of the charging opening at superheated temperature. Although all equipment was Class I, Group D, inerted or purged or intrinsically safe, a flash fire occurred that blew off most of the second floor explosion relief building siding and opened 22 sprinkler heads. There were no serious injuries and no structural damage.

Cause: Open kettle with chemical reaction above reaction temperature (improper procedure).

Preventive Measures: The initial reactant (alcohol) is no longer preheated in order to save reaction time. Also, the catalyst is withheld until it is the last item to be charged. A 100°F. safety factor below reaction temperature is now maintained and only loses 10 minutes in kettle heatup time over the previous speeded up procedure. Also, part of an instrument panel was moved to prevent the operator from being trapped and provide ready exit from the area of the reactor. The value of explosion relief siding was amply demonstrated.

CASE HISTORY NO. 995

Fire--Propane

Description; A tractor-semitrailer transporting 7000 gallons of propane caught fire after an external hose broke or ruptured while in transit. The drivers were attempting to shut off the escaping gas when it ignited. The accident resulted in the death of one driver and injuries to three other persons. In addition to the vehicle, fire damage extended to a two-story frame house and four other motor vehicles parked nearby. The accident occurred in a mixed residential and business district. At the time of the accident, the weather was clear and traffic was moderate. The cargo tank was 33 feet long and seven feet, four and three-eights inches in diameter, of frameless construction, with tank capacity 9526 gallons. The driver was accompanied by a driver-trainee. While at the shipper's plant, the driver attached the rubber hose from the propane cargo tank to the tractor fuel tank for the purpose of fueling the vehicle enroute. He stated that the hose appeared to have sufficient length to permit the vehicle to turn without damaging the hose or connections. Excess slack in the hose was taken up by looping a piece of wire around the hose and through a hole in the Fiberglass fender over the forward dual wheels of the tractor. The driver thought the wire would keep the hose from dropping to the wheels or binding, and the hose could move within the loop as necessary. Shortly after making a left turn (approaching the accident scene) there was a noise of escaping propane vapor. The driver stopped the vehicle, cut off the engine, and told the driver-trainee to shut the valve at the right fuel tank. The driver then attempted to reach under the cargo tank to shut off the hand control valve at the discharge line. When the driver-trainee touched the valve on the fuel tank, the vapors ignited, engulfing him in flames. He died five days later as a result of burns. The driver suffered serious, but less severe, burns and survived. The escaping gas continued to burn for approximately one hour and a half despite efforts of the city fire department, until the valve was finally shut off by an employee of the carrier, using protective clothing. Two bystanders were hospitalized from possible inhalation of fumes and shock.

Cause: Examination of the vehicle after the accident disclosed no defective mechanical condition with regard to the tractor which might have contributed to the occurrence; however, a modification in the external piping arrangement on the cargo tank definitely contributed to the accident. The tank was originally equipped with a three-inch discharge line located just aft of the landing gear, projecting from the center of the tank toward the curb side. This discharge line included an excess-flow valve at the other end of the line. The modification included the insertion of a T-joint between the excess-flow valve and the manual control valve in the discharge line. Into this joint was fitted a 1-1/4 inch pipe and hand cut-off valve which provided for a hose connection. A 3/4 inch rubber hose had been connected between this fitting and a fitting on the right fuel tank of the tractor. This arrangement, which bypassed the main discharge valve, permitted fueling of the tractor directly from the cargo tank. The excess-flow valve in the cargo tank, which had a rated capacity of 250 gallons-per-minute, provided the required protection for the three-inch discharge line. The liquid flow capacity of the auxiliary fuel line, restricted by valve and connections, was much lower, rendering the excess-flow valve ineffective. Thus, in the event of failure of the hose between the cargo and fuel tanks, the only means for controlling the flow of propane was the single manually-operated valve off the main discharge line. No secondary excess-flow protection was provided. Pressure relief valves located at the top of the cargo tank functioned properly during the fire.

Preventive Measures: A number of accidents, some with extremely serious consequences, have occurred in recent months in the transportation of liquefied petroleum gases by cargo tank vehicles. The nature and severity of these accidents have shown beyond question the hazardous nature of this commodity if not properly handled. This accident demonstrates the prime necessity for more adequate measures for instruction and supervision of drivers who are entrusted with the operation of vehicles transporting these materials. Proper control of the practices of drivers is an essential element in the responsibility of carriers.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 996

Benzoyl Peroxide Fire

Description: An operator was preparing to make a special mix. He was weighing out 1.6 lbs. of benzoyl peroxide into a large stainless steel beaker. As he picked up the beaker and turned away from the weigh station with it, the peroxide belched forth fire. The operator threw the beaker to the floor and quickly ran for a dry chemical extinguisher. With the help of the foreman who was close by, he managed to extinguish the blaze. By the time the operator reached the extinguisher, the peroxide had probably burnt itself up, but there was a small amount of methyl methacrylate in a pan underneath one of the pumps which was blazing.

An investigation showed that the operator had rinsed out his beaker with methyl methacrylate prior to weighing out the benzoyl peroxide. Even though he shook the beaker out, no doubt there was a small amount left in it which polymerized rapidly in contact with the peroxide resulting in a local build-up of heat and ignition of the catalyst. In the past the laboratory has weighed out practically all the benzoyl peroxide for the department. The operator had not received specific instructions on how to weigh up and add the catalyst to this mix which was a comparatively new operation for him. However, supervision had assumed that it would be done in the way that the master mixes were made.

The operator was astute enough to realize that the benzoyl peroxide should not be added to the mix in the dry form and was planning to slurry it with another ingredient. However, he did not understand the danger of rinsing the beaker out with methyl methacrylate prior to use. This is a standard cleaning procedure.

This was the third time this particular operator had weighed up this mix. The first two times he had not been rushed, and presumably the methyl methacrylate had had a chance to evaporate from the beaker prior to weighing up the benzoyl peroxide. The third time he was running late, and by his own admission, there was practically no delay between the time he cleaned out the beaker and weighed up the catalyst.

Preventive Measures:

1. A special beaker shall be used for weighing catalyst only.
2. More training will be given on the hazards of benzoyl peroxide. The Fire Marshal is going to present his demonstration again next month.
3. The benzoyl peroxide sheet in the Hazardous Chemical Manual will be revised to reflect more accurately the insidious nature of this material.
4. All other places in the plant which handle benzoyl peroxide will be studied to see that safe handling procedures are used at all times and that personnel are properly instructed in the hazards.
5. It is never necessary to weigh out more than one pound of peroxide since each package contains just exactly one pound.

CASE HISTORY NO. 997

Fire Occurs in Drum Storage Yard

Description: A fire occurred in a drum storage yard in which 800 steel drums (55 gallon) containing solvents and adhesives and three underground storage tanks containing some 36,500 gallons of solvents were housed. Most of the drums were stored in a horizontal position. The underground tanks were dual compartmented, horizontal steel tanks. The pumps to these tanks were located in pits (below ground level) adjacent to the tanks. The pits had interconnecting drains to a concrete covered sump at the south end of the pump pits. The switches to the pumps were located on an adjacent building wall.

The source of ignition has not been determined. Stories of eye witnesses concerning the point of origin differ between a drum or drums several feet from the pump houses. There was no activity in the yard at the time of the fire nor was there any electrical energy to the pumps. There were no transfers being made at the time. This being shift change time would substantiate the above conditions. A remote possibility of vandalism was discussed; however, no one was observed inside or outside the fenced area at the time.

Approximately 450 of the drums plus three pump houses and equipment were destroyed. The three underground storage tanks containing solvents were also affected and may be abandoned from further use. The estimated property loss, including the bulk solvents, was in excess of $100,000.

Causes:

1. Excessive storage of flammable solvents and adhesives.
2. Pump pits were known to have accumulations of solvent vapors due to leakage of the pumps.
3. Drums stored horizontally lost their entire contents when ruptured, which added to the spread of the fire. Close stacking of the drums also contributed.
4. Underground storage tanks were not equipped with approved flame arrestors. Vapors flashed and blew off fill caps and possibly contaminated the material.

Preventive Measures:

1. A clear space distance from drum storage to buildings of at least 50 feet should be maintained. This clear space should also be free of other combustible material accumulations.
2. Reduction of present inventory levels and controls on maximum levels to be permitted.
3. A method of cooling drums during high temperature weather conditions should be provided.
4. Horizontal versus vertical drum placement in accord with cooling and handling practices should be investigated.
5. Equipment should be provided for the application of mechanical air foam extinguishment for this class of fire.
5. Approved type flame arrestors and vents should be provided in bulk flammable liquid storage tanks.

CASE HISTORY NO. 998

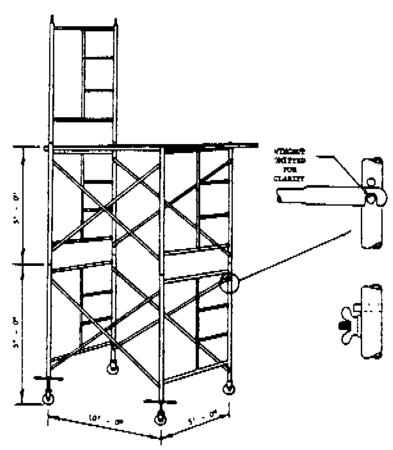
Employee Fatally Injured When Scaffold Collapsed

Description: An AEC contractor employee was climbing down the side of a rolling type scaffold. When he shifted his weight, the scaffold started to swing and, at the same time, fold together from a rectangular shape to an almost flat vertical shape.

Following the folding action, the scaffold began toppling. The employee held on until it was about halfway down. He landed on the concrete floor on his buttocks, rolled backward, striking his head, then either bounced up, or attempted to sit up, at the moment the scaffold fell on top of him. Part of the scaffold struck him a forceful blow on the face, knocking his head back down against the concrete floor, rendering him unconscious. He died, without regaining consciousness, six days later in the hospital.

The scaffold involved was made up of two 5-foot-high welded tubular steel sections, supported by a 6-inch caster with leveling screw on each of the four legs. Four cross braces held the end sections together, forming a 5-foot-wide by 10-foot-long by 10-foot-high scaffold on 6-inch casters. The leveling screws in two of the legs had been partially extended to compensate for a sloping floor on which the scaffold was being used. (See sketch)

Cause: Some of the scaffold deficiencies contributing to the accident were as follows:



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Only two planks (2 in. x 10 in. x 10 ft. and 2 in. x 10 in. x 14 ft.) without cleats were used for decking.

Eight of the sixteen wingnuts provided for securing the cross braces to the scaffold legs were loose. Some of the threaded studs were heavily crusted with fused metal from oxyacetylene cutting or rust and the wingnuts could not be turned. Also some cross brace locking studs were missing.

Two of the casters were not equipped with locking devices; the other two did have them but they were not locked. It was reported that assorted pieces of 2x4's and angle iron were used to block the casters.

The scaffold was not equipped with horizontal bracing, except for the bearers built into the end sections, nor was it equipped with guardrails, midrails and toeboards.

Preventive Measures: AEC Manual Chapter 0550, standards for Health, Safety and Fire Protection, lists the following standards for the safe construction, maintenance and use of scaffold equipment. In addition, and because of the differences between certain provisions contained in these standards or codes, paragraph 0550-054, Conflicts in Standards, was incorporated into the Manual Chapter stipulating that "...the standards providing the greater protection shall govern."

1. ASA A10.2 Safety Code for Building Construction.
2. Division of Industrial Safety Orders – State of California.
3. Minimum Safety Standard and Practices for the Building and Construction Industries – State of Idaho.
4. Safety Code and Amendments, Department of Labor and Industries – State of Washington.
5. Safety Requirements – U.S. Corps of Engineers.

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 999

Defective Pump

Description: An employee was engaged in routine duties as a pfleiderer pit man in No. 1 unit. He noticed the liquid level (mixture of 18 percent soda and water) in a floor sump near No. 4 crumb packer was too high. He proceeded to the sump and started the air sump pump by placing the ball valve in the "on" position. Soda and water gushed out of the air exhaust pipe and struck the employee in the face. He was not wearing goggles. He was by himself, and although standing very near both safety shower and eye wash fountain, was temporarily blinded and in extreme pain. He shouted for several minutes until help arrived. He suffered chemical burns of both eyes, face, lips, tongue, head, and neck.

Cause:

1. Insufficient supervision (employee was not instructed to wear goggles and the pump was known to be defective).

2. The pump was defective in that the liquid was leaking through the seal and being discharged through the air exhaust which is a straight section of pipe, not directed to the floor or other safe location. Moreover, only a week before a shift mechanic had received similar injuries in identical fashion. Severity was minimized in that he was wearing goggles. However, corrective action to replace pump was started but not followed through. Additionally, control valves originally were located a safe distance from pumps, but without authorization had been moved closer.

Preventive Measures:

1. Insure safe design of equipment and adequate maintenance.

2. Realistically survey and evaluate eye hazards, especially chemical, in all plant areas. Decide what eye protection must be worn as a secondary line of defense, either on a job or area basis, and insure that supervision both complies itself, and enforces the minimum regulations decided.

3. Above all, educate all employees on eye hazards, and stimulate them to safeguard themselves. Caustic of almost any concentration is a grave eye hazard.

CASE HISTORY NO. 1000

Acetic Acid Sampling

Description: A two-compartment trailer connected to a tractor and operated by a common carrier was delivering acetic acid to a plant. After the truck had been connected for unloading, the truck driver opened the top manhead on each of the two compartments. These were propped open by resting them on one or more of the lugs that are used to fasten the manheads closed.

Pumping of the acetic acid was started by one of the operators. After the pumping was started the operator climbed to the top of the trailer to obtain a routine sample from the forward compartment. To obtain the sample, he had to lift the manhead from the supporting lugs and open it wide. After the sample had been obtained, the manhead was reclosed. A few seconds after the manhead was closed the tank imploded.

After the tank collapsed the driver immediately closed the outlet valve on the bottom of the compartment. He then went to the top of the trailer and found the manhead cover on the forward compartment closed and held tightly by the vacuum. It appears that the operator, after getting his sample, let the manhead go completely closed instead of leaving it partially open.

Cause: The tank on this trailer was equipped with a spring loaded vacuum breaker on each compartment. Apparently this vacuum breaker either failed to open or was sized too small.

CASE HISTORY NO. 1001

Preplanning Minimizes Damage Following Liquid Hydrogen Turbopump Rupture

During test of gaseous hydrogen-driven turbine (used for operating a liquid hydrogen turbopump), gas pressure suddenly increased to approximately 1500 psi, causing the turbine casing to rupture and turbine disc segment ejection in the plane of the turbine rotation.

The accident is of interest primarily because of what did not happen. Test conditions involved anticipated flow rates up to 30 lbs. of hydrogen per second... rapidly enough to generate potentially over 150,000 cu. ft. of explosive gas (when mixed with air) per second. The area in which the test work was conducted was maintained under inert gas atmosphere so that, following hydrogen release during the accident, inadequate air was present to permit forming explosive mixtures. Further, immediately following the rupture, a variety of automatic safety controls functioned to terminate rapidly further hydrogen release, while other safety devices functioned to introduce an inert gas purge, preventing possible airflow into lines that had been used to handle the liquid hydrogen. Personnel performing test control activities utilize remote controls to permit conducting their work at a safe location, again a reflection of preplanning and hazard evaluation.

U.S. Atomic Energy Commission Case History

CASE HISTORY NO. 1002

Solid Composite Propellant Fire in Laboratory Mixer

Description: A 15-pound batch of ammonium perchlorate castable propellant was being mixed in a 2-1/4 gallon horizontal mixer. Upon charging the last propellant ingredient to the mixer, the operator left a 6 in. x 1/2 in. stainless steel spatula in the mixer bowl. Propellant ignition occurred shortly after restarting the mixer. There were no injuries. The deluge system functioned efficiently. Damage was slight, the cell was lightly soiled and a sheet plastic burn-out panel in the weak wall burned out.

Cause: The propellant was ignited by the friction and force generated by a metal spatula entering into the mixing action.

Preventive Measures: Laboratory operating personnel must now certify in writing that a mixing cell is free of extraneous items prior to starting a mix. They must list the tools taken into a mixer cell and must account by signature for each of these tools prior to each starting of the mixer.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1003

Truck Kills--"Standing Still"

Description: An auto tire company employee (non-AEC), arrived at an AEC contractor's plant gate to deliver tires and told the guard that he had only a few and was in a hurry.

A restricted area pass was prepared and a guard escort was assigned to accompany the tire man and his truck to the receiving dock. Arriving at the proper building, the tire man opened the tailgate, backed his truck into the dock and unloaded the tires onto a pallet. The receiving department employee then moved them inside the building and noted the tire man getting into the cab of his truck. As the receiving department employee was closing the warehouse door, he observed that the tire man had moved his truck forward 4 or 5 feet and was approaching the tailgate.

Cause: Following these events, the tire man apparently went in back of his truck and while closing the tailgate, the truck slowly drifted backwards until the right front wheel rolled off a raised pad (2 ft. x 4 ft. and 4 to 6 inches high) for dolly wheels on semi-trailers, causing a sudden backward surge by the truck which pinned the tire man between the dock and the truck.

The guard escort, in a patrol car, had backed around to a position heading toward the gate, and was on the opposite side of the truck from the tire man; thus, did not see what was happening.

Almost simultaneously, another car with two contractor employees drove into the immediate vicinity. These two men realized immediately what was happening, jumped out of their car, one going to the tire man's aid and the other calling to the guard to radio for the ambulance, and at the same time getting into the truck cab to move it forward to free the tire man. (The truck motor was running and the brake was on - but apparently not tight enough to hold.)

The victim was promptly transported to the contractor's hospital and later to a private hospital in a nearby town, where he died as a result of severe internal injuries about 12 hours after the accident.

U.S. Atomic Energy Commission Case History.

CASE HISTORY NO. 1004

Furnace Inspection

Description: Two men entered a rotary furnace to inspect the burner tip. The furnace had been shut down five days previous and the fires left to die. The two employees were walking on top of the soot-cinder accumulation in the bottom of the furnace. The heavier man broke through the crust and into hot ashes in the bottom. Injuries consisted of first and second degree burns to both legs between the ankle and knee.

Preventive Measures:

1. Whenever personnel must enter a furnace or firebox, sufficient planks will be placed to make a safe platform.
2. The ash residue will be probed for the presence of hot ashes or embers which would require quenching and/or special clothing.

CASE HISTORY NO. 1005

Fire--Powder Buggies

Description: Fire destroyed three powder buggies and floor of a tram track. The unattended truck carrying three empty buggies was standing in bright sunlight on the track away from any process building when flames were noticed. The fire was allowed to burn out with no further damage.

Cause: The truckers had placed three one-gallon glass containers, partially filled with alcohol, in one of the buggies to be used later in routine "clean-up" procedure on Gelatin machinery. They left the truck standing in bright sunlight. We believe the conditions were such that the position of sun and bottles were just right for a lens effect through the glass to concentrate sufficient heat on the surface of the buggy to start a fire.

Preventive Measures: Immediate removal of all glass containers from not only the explosive area but from the entire plant area, and prohibiting the use of glass containers for any purpose.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1006

Lack of Clear Instructions

Description: A machine tender was assisting a foreman in checking and cleaning out a stock pump that was running hot in the basement of a machine room. The employee misunderstood the foreman's instructions and had his right hand in the "cleanout opening" when the foreman started the pump.

The foreman stated that he was going upstairs to start the pump to listen for a metal object as they both agreed that this might be the source of trouble. It was at this time that the machine tender removed the hose from the cleanout opening and reached in just as the pump was put in operation. His injuries consisted of an amputation of the second finger of the right hand at the first joint and a possible fracture of the ring finger.

Preventive Measures:

1. In the future, no machine room employee is to put his hand into a stock pump unless the power has been cut off and the operating switch "tagged" or "locked out." The foreman should stay with such equipment until repairs have been made and equipment started.
2. The great importance of being certain that instructions are always "clear" and "understood" will be stressed with all machine room personnel.

CASE HISTORY NO. 1007

Shocked When Washed-Down Electrical Equipment Is Contacted

Description: The shift operator on day shift at the Stengel operation received a strong electrical shock at the Compactor when he took hold of the cable leading to the bagger foot switch. The bulk flow had been washed down and the floor had some water and wet ammonium nitrate on it. The foot pedal and cable had been laid on the conveyor during washdown. On starting up, the pedal and cable were placed on the floor and the cable was tangled under the empty bag box. A bag was being filled when the operator reached down and grasped the cable about four feet from the pedal. He immediately received a continuous electrical shock which numbed him, threw him against the wall and kept him from releasing the cable. The current flow ceased when the bag on the bagger was filled to capacity and the bagger door snapped shut. Operator had to be helped outside the bagging room where he quickly recovered.

Cause: At the time of the shock the operator was not grasping any metal but his feet and shoes were wet with ammonium nitrate solution. Moisture was found in the pedal and around the cable at the switch. The cable was wet on the outside along its whole length.

Preventive Measures:

1. Installation changed to permanent conduit and switch relocated to prevent moisture exposure.

2. Ground system improved to prevent breakdown.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1008

Runaway Chemical Reaction

Description: This incident occurred in running a "SKRAUP" reaction for producing quinoline. Ingredients consisted of aniline, glycerine, nitrobenzene, ferrous sulfate, sulfuric acid, and water.

The reaction had been run many times previously without trouble. This, however, was the first 100-gallon batch run, previous runs had been 50 gallons. The reaction was conducted in a 200-gallon, glass-lined jacketed reactor with agitator and a six-inch rupture disc in a six-inch vent line extending above the roof. There was a Pyrex glass condenser connected to the vent line.

When sulfuric acid was added, the reaction appeared to start immediately without added heat. It was being watched closely when material was seen erupting into the glass condenser. At this point the operators left the building. Just as they arrived in the street, the rupture disc blew, causing a mist cloud to be projected out of the vent pipe. Shortly after this, the manhole cover blew off. Most of the contents of the vessel erupted, striking the underside of the roof with enough force to break several lightweight concrete slabs.

The material discharged from the vent created a skin and respiratory hazard in the immediate area. Sprinklers were knocked open manually and allowed to run several hours to wash down the building interior. The exterior of plant buildings and also residences in the nearby area were washed down with spray nozzles by the plant fire department.

Medical Department checks were made. There were symptoms of minor cyanosis but there were no real injuries - all symptoms cleared up promptly.

Cause: Investigation indicates that there was an excess of sulfuric acid. Due to warm weather, temperatures were higher than usual, the ingredients being at 32°C when the sulfuric acid was added. It is also possible that some of the ferrous sulfate may have settled out to the point where it was not picked up by the agitator as all materials except the sulfuric acid were in the reactor over the weekend. This is somewhat unlikely as the ferrous sulfate disperses into the other materials and does not readily settle out.

The reaction is known to be sensitive to water content. Water acts to slow down the reaction and may be used as a quench. The ferrous sulfate is also an inhibitor. Excess sulfuric acid will increase the rate of reaction.

The incident raises questions in regard to the sizing and rating of rupture discs. Apparently there are some situations where a rupture disc of any reasonable size may not be effective.

Subsequent experiments have shown that the heat of dilution of the excess sulfuric acid causes the mixture to reach a critical temperature of 120°C immediately, particularly if started above 30°.

The operator unintentionally added more than the planned amount of sulfuric acid.

CASE HISTORY NO. 1009

Acid Sampling

Description: An employee was preparing to take a sulfuric acid sample at a still location. When he opened the one-fourth inch sampling line cock, the acid spurted onto the ground, and splashed on the employee. One of the leg burns he sustained became infected, and the employee had to be hospitalized.

Cause: The flow of acid from the sampling line was difficult to control with the type cock used.

Preventive Measures: A wheel-controlled sampling valve to more effectively control acid flow from the sampling line has been installed.

Employees will wear face shields in addition to splash goggles while taking samples.

CASE HISTORY NO. 1010

Explosion -HNF Manufacture

Description: Two violent decompositions (fume-off) of nitrogen followed by explosions occurred during manufacture of hydrazine nitroformate. No personnel were injured. Loss of equipment was limited to one ice chest. Approximately 20 pounds of NF were involved in the incident. The initial decomposition occurred near the crystallization shed and involved one polyethylene bottle containing approximately 11 pounds of a 90% NF-10% isopropanol solution. After the first explosion, the remaining 5 bottles of NF, one of which contained 10% isopropanol, were placed in the ice chest located near the operating area. The second explosion is believed to have been caused by the one bottle containing the NF - isopropanol solution. All of the nitroform involved had been previously frozen and was being thawed for an HNF reaction. The material was stored frozen and considered to be safe based on samples of frozen NF stored for approximately 1-1/2 years with periodic thawing. This material showed no signs of deterioration.

Cause: Subsequent investigation and tests revealed the following:

1. When nitroform is dissolved in isopropanol forming solutions wherein the concentration by weight of nitroform is 50% or greater, an exotherm is observed. This exotherm increases directly with the concentration of nitroform above 50% by weight.

2. Nitroform is very reactive with HNO_3 and its constituents, some of which may have been present in the nitroform used at the time of the incident.

3. Nitroform is more stable when frozen and is stored for short periods in this state. The nitroform that was reacted the day of the incident with isopropanol was still partially frozen. In addition to the exotherm that is known to occur under the conditions of paragraph 1 above, nitroform goes into solution exothermically which may also have contributed to the incident.

Preventive Measures:

1. Prior to further reaction, all of the nitroform will be completely thawed.

2. The pH of the nitroform will be more closely controlled to minimize the possibility of HNO_3 or its products being present.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1011

Tank Collapse

Description: A two-compartment trailer connected to a tractor and operated by a common carrier was delivering acetic acid to a plant. After the truck had been connected for unloading, the truck driver opened the top manhead on each of the two compartments. These were propped open by resting them on one or more of the lugs that are used to fasten the manheads closed.

Pumping of the acetic acid was started by one of the operators. After the pumping was started, the operator climbed to the top of the trailer to obtain a routine sample from the forward compartment. To obtain the sample, he had to lift the manhead from the supporting lugs and open it wide. After the sample had been obtained, the manhead was reclosed. A few seconds after the manhead was closed the tank imploded.

After the tank collapsed the driver immediately closed the outlet valve on the bottom of the compartment. He then went to the top of the trailer and found the manhead cover on the forward compartment closed and held tightly by the vacuum. It appears that the operator, after getting his sample, let the manhead go completely closed instead of leaving it partially open.

Cause: The tank on this trailer was equipped with a spring loaded vacuum breaker on each compartment. Apparently this vacuum breaker either failed to open or was sized too small.

CASE HISTORY NO. 1012

Removing Blank Flange from Line-- Sprayed with Acid

Description: The injured employee and a co-worker were removing a blank flange from a one-inch sulfuric acid line. This was in preparation of hooking up a sump pump. The two bolts in the blank flange were removed; however, the blank was still held in place by the sticking of the gasket. The injured employee was sprayed with sulfuric acid when the blank suddenly broke loose after being tapped with a crescent wrench. He received severe chemical burns to the forehead, lips, chin, and neck.

Cause:

1. There was a low spot in the line that contained 94 percent sulfuric acid.

2. The employee did not take adequate precautions for breaking the line because he was not aware of the hazard.

Preventive Measures: 1. The discharge line will be modified to minimize the low spot in the line.

2. The department will develop a minimum safety procedure for opening lines. A plant-wide minimum procedure for the opening of lines should also be developed.

3. All employees will be alerted to the fact that all lines to be opened must be treated as though they are under pressure.

CASE HISTORY NO. 1013

Steam Pot Used as Flask Holder Spells Fire Hazard

Description: A chemist set a 22 liter flask containing 12 liters of a filtrate on a steam pot as a holder for the flask and left the laboratory. The filtrate contained diethyl ether and benzene. Although the chemist did not wish to heat the filtrate, the steam valve connected to the steam pot was in need of maintenance and was leaking.

A second chemist, shortly afterward walked past the flask and also left the lab. He claims he did not smell ether or benzene when he passed the set-up and no one else was in the laboratory.

"A minute or so later" an explosion and fire occurred opening the explosion vents and 10 sprinkler heads.

Cause: It is believed that the steam vaporized some of the ether and benzene releasing the vapors into the room where they reached a source of ignition such as an arcing Powerstat or an electric mantle. A Powerstat was located 4-1/2 feet above the floor and about 5 feet from the flask.

Preventive Measures: 1. Defective equipment and services should be reported and repaired immediately.

2. Hand rubber flask holders should be used instead of steam pots.

3. Sparking devices should not be used in the vicinity where flammable solvents are handled unless they are suitably protected to prevent the sparks from becoming a source of ignition.

CASE HISTORY NO. 1014

Worker Injured by Metal Eel

Description: A Leadburner Helper and a co-worker were using a metal eel to unstop a cascade line. An end of the eel struck the injured on the cheek and eye.

Cause: Employee was not wearing eye protection at the time of the accident due to heat and humidity causing goggles to fog rapidly.

Preventive Measures: 1. Continue to stress the importance of goggles when performing jobs of this type. Effort will be continued to obtain alternative types of eye protection that will not fog as badly.

2. Enforce existing eye protection regulations.

CASE HISTORY NO. 1015

Lock and Tag Procedure Ignored

Description: A Utility Man was using a tool to turn feed roll motor on staple machine for cleaning. He called to a co-worker who was standing by the switch, "Don't start motor." The co-worker misunderstood the order and started the motor. The Utility Man was holding the tool and when the motor started, his arm struck the bottom edge of the metal guard.

Preventive Measures: Follow written lock- and tag-out instructions when working on electric motor-driven equipment.

CASE HISTORY NO. 1016

Spool Piece Sight Glass Failure--Fire

Description: A flash fire occurred at the base of an alpha Picoline recovery still. No damage to property or injury to personnel resulted from the fire.

Cause: The cause of the fire was a combination of unusual circumstances. During the distillation a crack due to vibration of a recycle pump developed in a two-inch Pyrex spool piece on the discharge side of the pump, releasing the solvent into the area. The spray of solvent came in contact with an energized electric welder starter switch which caused an arcing that resulted in the flash fire. The welding machine was not in use at the time and had not been used for approximately a week, however, it was left plugged into a 440-volt circuit close to the recovery operation.

Preventive Measures: To prevent a recurrence, specific instructions have been issued on the safe use, and storage of welding machines and similar equipment. The spool piece sight glass has been replaced by a metal enclosed bull's eye.

CASE HISTORY NO. 1017

Sodium Isopropylate Fire

Description: A plant fireman was injured and hospitalized for second degree burns received when flammable vapors reflashed while fighting a fire in a vitamin operation. Property damage is estimated at $20,000 to $25,000. The fire occurred in an isolated room where Sodium Isopropylate is prepared but later spread through a wall opening to the main operating area and activated 55 sprinklers. It took more than an hour before the emergency was completely under control.

The Sodium Isopropylate normally is blown by nitrogen pressure to another vessel in the main operating area via an oil heated line. This line plugged because of problems with an air operated addition valve on the line, and the piping had to be dismantled. While the line was being dismantled the Sodium Isopropylate was kept warm in the reactor.

Cause: Personnel had failed to close a valve on the dismantled line at the reactor, and eventually pressure built up causing material to come out of the line into the "cubicle" and into the main operating area through the opening in the cubicle wall where a portion of pipe had been removed.

Preventive Measures: Manually operated sprinklers will be installed in the cubicle and the plant is reviewing all sodium reaction installations with respect to fire extinguishment.

CASE HISTORY NO. 1018

Phenol Fatalities

The severe hazards of phenol are illustrated by the following three fatal incidents. Case history (c) below is excerpted from a report by the Association of British Chemical Manufacturers taken from "Sichere Chemiearbeit."

(a) A research chemist carrying a pail of phenol slipped and fell. Although the phenol which splashed on him was washed away at once, he died twenty minutes later.

(b) Phenol was being pumped through a filter and, inadvertently against a closed valve. The filter failed and a mechanic working on the system was sprayed. Although he was showered immediately, he collapsed and was D.O.A. at hospital.

(c) A mixture of carbolic acid and methylene chloride was produced in a paint and varnish factory. The carbolic acid, consisting of 90 per cent phenol and 10 per cent water, totalling 170 kg., was supplied in casks and poured into a vat provided with stirring apparatus, in which there was already 830 kg. methylene chloride.

In the pouring process it appears that a worker was so unfortunate as to pour the carbolic acid over himself. Large parts of his body, such as his chest, head, sides and arms were very much reddened. Comrades who hurried to his assistance treated him with alcohol and soapy water. He was soon sent to hospital and died the same day. Collapse of the circulation was ascertained to be the cause of death. No witnesses were present at the accident. The injured man himself did not give any account of the accident. On subsequently weighing the mixture it was discovered that only a few kilogrammes of liquid had been poured into the space.

The stirring apparatus container was covered with two half-lids, with a diameter of approximately 2 m. One half-lid was found in the container. It may therefore be presumed that the worker, in attempting to cover the container, fell with the half-lid into the container, which was only 1.50 m. deep, and immediately climbed out again.

It is well known that phenol and its solutions (carbolic acid), and likewise cresol, can cause poisoning of the whole organism, apart from the cauterization of the skin. Even if only fairly small areas of the body, such as a hand or arm, are affected, serious and possibly fatal poisoning may result.

Treatment of an injured person with alcohol is correct if only small areas of the skin are affected. If larger areas of the body are treated, the quantity of alcohol available is generally not sufficient. The part of the skin contaminated by phenol is then spread by rubbing with alcohol and increased, so that absorption through the skin is facilitated. In such cases only spraying with water can really be recommended, which can be allowed to operate for a long time (10 minutes). To avoid chills (pneumonia), the spraying should be at a certain temperature.

Note: The following statements are taken from the MCA Chemical Safety Data Sheet SD-4, Phenol 1964):

From 10.1.2 Acute Toxicity

"Collapse and death may occur in a few minutes after massive exposure despite prompt emergency care."

From 5.2.2.5

"Clothing made of neoprene or other impervious material may be worn to protect the body against phenol splashes."

CASE HISTORY NO. 1019

Drum Eruption

Description: Three maintenance employees were in the area working on a piping job. The welders had just cut a hole in a water pipe and the pipefitters were waiting for the water to drain. A drum of 66 Deg. Sulfuric Acid was setting on a nearby pallet. (The drum of acid was not a part of the job involved.)

Suddenly, and without warning, the drum erupted and 66 Deg. Be' Sulfuric Acid sprayed over the area including the three men.

Two of the men went to a safety shower in the Nash pump area nearby and proceeded to shower and discard their clothes. The other who was hardest hit was unable to immediately locate a shower. He was led to a shower in the DeNora Cell House by employees who happened on the scene at that time.

The Safety Office was notified of the incident and dispatched further help to the scene immediately. It should be mentioned at this point that the emergency number was not used in reporting this accident. However, there was no delay in making connections through the normal channel on this particular incident.

Cause: It is the opinion of the Investigating Committee that the drum erupted due to hydrogen pressure which had apparently been building up in this drum for some time. Since the drum of acid was in no way involved in the job being done in this area, it was purely a coincidence that the accident happened at the particular time the three people involved were in the vicinity.

During the course of the investigation, the following facts were brought to light:

1. The drum involved is a black iron ICC 5A - 14 gauge drum which is normally used to handle 66 Deg. Be' Sulfuric Acid.

2. It was purchased and delivered to Dept. 232 from the warehouse in February along with two other drums. The supplier does not have a record of when this drum was filled.

3. The other two drums were used but this one had not been opened and no evidence could be found that it had been vented. A label on the drum states that it should be vented weekly and should not be stored in direct sun.

4. The drum did not appear to be in good condition. This was verified by measuring the thickness of the bottom of the drum where it was split. The thickness ran from .028 in. to .050 in. with most of the metal being about .040 in. The normal thickness of 14 gauge drum steel is .0725 in. The supplier says each drum is tested by standard MCA weight test before filling. If drum has lost 15% of its original weight, it is not refilled.

It is recognized that the condition of the drum did not cause the accident but was a contributing factor.

Preventive Measures:

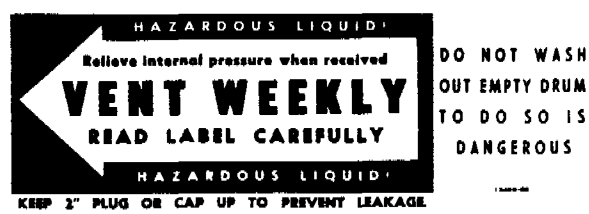
1. Obtain gummed Kum-Kleen type labels to be put on drum heads when they are received in the plant. The label should be designed so as to attract attention and should provide space for recording the date each particular drum was last vented and this should be done weekly. When drums are shipped to departments, a new label should be put on showing the last date the drum was vented.

2. Each manufacturing group survey materials they handle in drums which could cause a similar incident and furnish this list to the warehouse so a venting tag can be applied.

3. Each department handling drummed material requiring periodic venting to establish a procedure to assure that such venting is done on a weekly basis and that all personnel in their departments are acquainted with the purpose and use of the venting tags. The production department responsibility starts when drums are received from the warehouse. When drums are empty the tags should be so marked.

4. Review in departmental safety meetings the procedure for using the emergency telephone line to the dispensary and the importance of knowing the location of nearby safety showers while working in a certain area. This last recommendation is of particular interest to the shop people who are more likely to be working in unfamiliar areas.

Editor's Note: One company's "Venting label" is reproduced as follows:



CASE HISTORY NO. 1020

Improper Work Method

Description: An employee was attempting to take a sample of Butylether from a tank truck when he dropped the bottle into the tank compartment. He then requested the truck driver to pull forward, while he bent over the loading hatch, so that he could retrieve the bottle if the movement of the liquid brought the bottle near the hatch.

The driver pulled forward and applied his brakes hard, causing the liquid to splash on the head, face and shoulders of the employee. A water hose was used to wash the chemical off. The employee also changed clothes immediately. Injuries consisted of chemical burns to both eyes, similar in nature to a welding flashburn.

Cause: Investigation revealed the cause of the accident to be improper method of retrieving sample bottle and unsafe procedure.

1. Truck was moved while employee was still on tank.
2. Truck was moved with hatch cover open.
3. Employee was not wearing chemical goggles.

Preventive Measures:

1. Rules concerning the safety loading of tank trucks will be rigidly enforced.
2. A letter of reprimand is to be issued to the employee for violation of safety rules.
3. This incident will be discussed in all safety meetings.

CASE HISTORY NO. 1021

Hose Failure

Description: The ammonia loading hose at the tank car loading rack ruptured while loading an ammonia tank car. The operator closed the valve on the line to the tank car, but the tank car was not equipped with excess flow valves so ammonia continued flowing from the ruptured hose across the dome of the tank car. By using a car jack, the car was jacked south on the track until the blowing ammonia was no longer directly on the car dome. Firewater was sprayed on the leak while the operator closed the valve on the car. Approximately four tons of ammonia were lost; but, due to the wind direction, no operating area of the plant was endangered.

Cause: Equipment failure; this hose had not been in service long and evidently was faulty. It is a 600# ammonia hose and the pressure to the car was approximately 150#.

Preventive Measures:

1. Each hose should be tagged with a metal tag showing date of installation and also tagged at each pressure test. Hoses should be pressure tested every three months at 350# and replaced at the end of a year's service.
2. Investigate possibility of replacing existing tank car loading hoses with chicksan joints and pipe as Muscatine plant is using.
3. Install excess flow valves at all ammonia loading points.
4. Install excess flow valves in all MLUX tank cars in service. The fact that many MLUX cars in NH_3 service are not equipped with excess flow valves should be called to the attention of the central traffic office and recommendations made that all these cars be so equipped.
5. A fire hydrant should be installed near the south end of the scale tank shed to be another source of water for emergency use.
6. For temporary protection purchase excess flow valves to be attached to loading hose where it attaches to tank car valve when loading cars.

CASE HISTORY NO. 1022

Glass Ampoule

Description: A technician, in preparing to open a sealed glass ampoule containing 100 grams of anhydrous ethylamine, placed the bottle in a pan containing a slurry of dry ice in acetone which was located in a hood. Cooling was necessary prior to opening the sealed container because of the low boiling point of ethylamine (16°C). Upon contact of the ampoule with the dry ice slurry the bottle cracked, emptying the contents of the ethylamine at room temperature into the slurry causing a vigorous evolution of a mixture of ethylamine, carbon dioxide and cold acetone (at approximately minus 60°C). This mixture splashed onto the injured's face. She first attempted to cross the lab and wash her face under the tap, but had difficulty in seeing her way. A chemist, who at the time of the accident was at his desk in the laboratory, quickly guided her to the overhead safety shower in the hall immediately outside the lab. After thorough washing, she was taken to the dispensary, treated and then transported by ambulance to the hospital for further treatment and examination.

Cause:

1. Sudden chilling of the soft glass ampoule by the dry ice-acetone mixture caused the bottle to break as a result of thermal shock. The sudden mixing of the warm ethylamine with the cold dry ice slurry then caused the vigorous evolution leading to the injury.

2. Failure to wear eye protective equipment.

Preventive Measures.

1. Containers made of soft glass must never be subjected to excessive thermal shock. Excessive thermal shocks, as evidenced in this instance, can be avoided by moderate cooling by means of ice-water, ice-salt or ice-acetone mixtures or by gradual cooling in a refrigerator.
2. In operations of opening sealed ampoules which are likely to be under pressure, not only should goggles be worn but serious consideration should be given to wearing a face shield as added protection.
3. Group Leaders should review this report with all personnel and re-emphasize continued use of adequate eye protection in all laboratories.

CASE HISTORY NO. 1023

Operating Tractor in Inadequately Ventilated Area

Description: A tractor operator was unloading scrap metal from a box car located in a scrap building with a gasoline tractor equipped with a scoop. The unloading operator took approximately one hour. The employee reported to Medical later in the day complaining of a headache. He was examined and hospitalized for carbon monoxide poisoning.

Preventive Measures:

1. The tractor has been converted from gasoline to L.P. gas.
2. If it becomes necessary to use a gasoline tractor in a boxcar, both doors will be opened and a blower used in the car.

CASE HISTORY NO. 1024

Assumed Line Was "Clear"

Description: An employee was removing a spool piece from a monochloroacetic acid line. This was in preparation for repairing a small hole. To do this, the employee removed the bolts from the flanges. Standing on two adjacent pipe flanges, he attempted to separate the line; but the spool piece "stuck." To free the spool piece, he placed one foot on the bottom flange of the spool piece and moved the line sideways. As the line separated, about a cup of material splashed out onto his feet and legs. Chemical burns to both feet required hospitalization for skin grafting.

Cause:

1. The spool piece contained about a cup of liquid chloroacetic acid because the dip pipe directly below was frozen. The spool piece being traced kept the material a liquid.
2. The line was not checked just prior to the start of the job because it had been blown clear three days previous.
3. The employee placed his foot on the bottom flange of the spool piece to free it from the line.
4. The employee did not wear adequate personal protective equipment or wrap a covering around the flange to be broken because he thought the line was clean.

Preventive Measures:

1. Jobs will be checked prior to the start of work to determine the condition of the job at that time.
2. Individual responsibility for safety will again be stressed to all employees.
3. The wearing of adequate protective equipment will be stated on the job "work permit" and will be communicated to all foremen and workmen involved.

CASE HISTORY NO. 1025

Flammable Solvents--Electric Motor

Description: A minor surge in the solvent flow to a still had resulted, through interlocks, in a compressor shut-down. Instead of waiting until normal levels were re-established by draining through an automatic valve, operator cracked a bleed valve permitting highly flammable solvents, at about 100 lb. pressure, to bleed to the floor. After two attempts to start the compressor between bleedings, the operator was joined by another operator who opened the bleed valve wider while the first operator pushed the butterfly starting switch some 16 feet away. On the second large bleed (about 1/2 to 1 gallon) the cloud of vapors ignited as the compressor was being started, burning the operator about the head and right arm. His safety glasses protected his eyes.

Cause: The hazard of the normally high internal temperature of electric motors from repeated startings in a relatively short time was not generally recognized as an ignition source; and, the area operating rules limiting the starting of this motor to once every ten minutes or not more than three attempts per hour were, in practice, generally disregarded.

Preventive Measures: 1. All flammable solvent bleed points requiring frequent draining of more than a small quantity will be piped to a flare header.

2. Other bleed points will be provided with piping to drain into grounded safety cans, and small "spills" will be flushed with water.

3. Thorough review of procedures for starting electric motors and for handling flammable solvents will be given all operating employees.

4. Design of the controls and piping in this area will be revised for simpler operation.

CASE HISTORY NO. 1026

Water Trapped in Salt Bath

Description: A batch of "Hitec" heat transfer salt was being degraded (in a development laboratory) for subsequent corrosion tests by contacting molten salt with steam. The salt was in a 6 in. diameter x 20-1/2 in. long stainless steel pipe having six 1800-watt resistance heaters strapped to the outside and a water-feed line of stainless steel extending to the bottom of the tank where it was bent into a horizontal ring perforated with three sparging holes. Eight days after the operation was started, a fault developed in the electric power supply to the unit. After repairs on the next day, heat was reapplied. When the temperature of the bath reached about 350°C. at the center (although the bottom was still below the salt freezing point), the agitator was started and almost immediately two-thirds of the contents erupted from the container, some of it contacting two employees, setting fire to their clothing. They both sustained severe burns on anterior body surface from head to knees; fortunately they were wearing side shield safety spectacles which protected their eyes.

Cause: While heat was not being applied during repairs, the material froze to the point of blocking the sparge holes at the bottom of the water line. Extra water had been drawn into the top of the line when condensation of steam created a partial vacuum. The valve at the intake end of the water line was closed before heat was reapplied. This trapped water created steam pressure during heating, and resulted in violent ejection when material blocking the sparge holes melted.

Preventive Measures: Equipment and procedures are being revised to minimize exposure of employees when working with molten salt baths.

CASE HISTORY NO. 1027

Preparing Molten Sulfur Tank Car For Unloading

Description: The injured employee was preparing a molten sulfur tank car for unloading. The first step in this procedure is to make sure the unloading line is clear. To do this, the employee hand drilled down through the crust that had formed in the unloading line during transit. As the drill broke through the crust into the vapor space of the tank car, hydrogen sulfide gas was released. In attempting to get away from the gas, he started to climb down the ladder of the car. Part way down the ladder, he passed out and fell to the ground. He received multiple contusions to his face and upper trunk, plus a strain of the neck and shoulders.

Cause: 1. The vapor space in the tank car was filled with hydrogen sulfide formed by impurities in the molten sulfur.

2. The platform of the tank car was not aligned with the catwalk of the loading station because it was not designed to handle this type of car.

3. The operator was following established departmental procedures. The need for respiratory protection was not recognized.

Preventive Measures: 1. The loading station and unloading line will be redesigned to handle various types of molten sulfur tank cars.

2. A scrubber system will be designed to handle the hydrogen sulfide vented from tank cars and the storage tank.

3. Respiratory protection will be worn while cars are being drilled until the scrubbers are installed.

4. Work will be done with suppliers to eliminate the need to drill the unloading line.

5. Supervision will review the hazards of all materials handled in their department to assure proper handling procedures.

CASE HISTORY NO. 1028

Corrosive Liquid Burn

Description: An operator in the Amines Department was preparing to circulate the monoisopropylamine (MIPA) in No. 2 Batch Tank prior to taking a sample. He opened the suction and discharge valves of the pump and started the pump. As he removed his hand from the pump motor switch, he struck the handle of the ball-valve on the pressure gauge vent line. The valve "cracked" open and MIPA sprayed onto the right side of his head, face and body. The exposure to the MIPA (99%) resulted in chemical burns to the right side of his face, severe irritation to his right eye and minor irritation to his left eye, head and body. The employee was wearing prescribed safety equipment—safety hat, safety spectacles and gloves. The employee was hospitalized for several days, however, he sustained no permanent damage to his eyes.

Cause:

1. The vent line from the pressure gauge normally is not under pressure, however, after the pump was started there was approximately 28 psig of fluid pressure in the line.

2. The accident resulted from the accidental opening of a pressurized line.

3. The ball-valve is a quick-opening type of valve, easily operated and is subject to being accidentally opened.

4. The discharge of the vent line is horizontal and at head level.

Preventive Measures:

1. All vent lines, and other open end lines, controlled by ball-valves will be fitted with an elbow so that the discharge from the line will be downward. The ends of the elbow will be capped to prevent accidental discharge.

2. A modification of the ball-valve will be made so that the valve handle may be removed. A "master" handle will be carried by the operator.

CASE HISTORY NO. 1029

Improper Shut-Down Procedure

Description: Trisodium phosphate (TSD) slurry at 194°F was being pumped through a stainless steel line to a furnace when a leak developed in a gum rubber gasket between one of the flanges. The equipment was then ordered to be shut down to repair the leak. 120 pound 340°F steam was introduced to blow down the system, but valves were left partially closed which over pressured the system and blew the hot slurry on the operator in the midsection area. He received second degree burns.

Preventive Measures:

1. Review the details of this accident with all furnace operators.

2. Investigate when steam pressure can be reduced to meet the requirements of the process and eliminate unnecessary high pressure.

3. Continue efforts to eliminate leaks at flange connections by selection of better gasket material.

4. Examine lines to see if any flange joints can be eliminated.

5. Investigate further use of flange guards.

CASE HISTORY NO. 1030

Two Fires in Polymer Dryer

(a) Description: Water-wet polymer was being dried by circulating hot air in a steam-heated continuous dryer that was approximately 10 feet high by 10 feet wide by 84 feet in length. Near the end of the afternoon shift an operator saw smoke coming from the outlet end of the dryer and simultaneously smoke was observed at the opposite end near the top of the access doors. Shortly thereafter flames erupted from several openings. A fire alarm was turned in at the first sign of smoke, the flow of polymer to the dryer was stopped, circulating fans and exhaust fans were shut down and all electrical equipment was de-energized.

As room air was exhausted only through the dryer exhaust fans, the area quickly filled with dense black smoke and fumes from the burning polymer. The use of 2-1/2 inch hose lines from outside hydrants was delayed until the private fire brigade could put on self-contained breathing apparatus for respiratory protection. Interconnection of exhaust ducts between dryers, and polymer dust that had accumulated in an idle duct allowed fire to spread beyond the first dryer. When fire burned through the aluminum exhaust ducts, 14 automatic sprinkler heads at the ceiling opened and held the fire in check until it was extinguished with hose lines. The dryer, circulating fans, exhaust fans, and continuous belt were heavily damaged, especially in the center section. A fire extinguishing system had not been installed within the dryer and it had been operated for 12 years without incident.

Cause: A short section of V-belt looped over the exterior belt driven circulating fan drive pulley had been used for a number of years to stop the fan from "windmilling" when the motor circuit was de-energized for operating or mechanical reasons. Charred pieces of this "brake belt" were found in the annulus around the fan shaft and apparently ignited a quantity of dry polymer that had accumulated at this spot. Once ignited, air movement spread burning polymer throughout the enclosed dryer.

Preventive Measures: All brake belts were removed from all dryers. Idle ductwork and exhaust fans were removed and interconnecting ducts provided with fire dampers.

(b) Description: Two weeks after the fire reported in (a) an odor of burned polymer was noticed around another dryer and shortly afterwards smoke was observed coming from the top of the doors on the side of the dryer and from the exhaust duct on top of the dryer building. Personnel outside the building, seeing the smoke, turned in the fire alarm. The flow of polymer to the dryer was stopped and all fans and electrical equipment were immediately de-energized. Dense smoke and fumes filled the room and it was necessary for the private fire brigade to use self-contained breathing apparatus in order to extinguish the fire with hand extinguishers and 2-1/2 inch hose lines connected to yard hydrants and to the plant fire truck.

In this instance, because of early shutdown of all fans, damage was confined to the dryer and the overhead ductwork was not affected. Automatic sprinklers installed in the building did not operate as room temperatures were not high enough to fuse the heads.

Cause: As the most severe damage was in the center of the dryer, a thorough investigation, including piece by piece dismantlement, was made of this section. It was found that one of the circulating fan bearings failed prior to the fire and the metal insulation shroud around the fan shaft was dislodged so that it blocked passage of air through the steam coil. As a result, polymer accumulated in the coil and was subjected to auto-decomposition due to higher temperatures in the area where passage of air was blocked. Ignition of decomposition products could have been caused by either a spark or auto-ignition of the polymer, or of the dryer belt lubricant.

Preventive Measures: All existing and replacement polymer dryers will be equipped with automatic fire detection, automatic shutdown and automatic extinguishing systems and an overriding emergency button will be provided to manually shut down the dryer and auxiliaries and to actuate the extinguishing system. Dryers will be modified to minimize polymer traps and to facilitate inspection and cleaning. Dryers will not be operated with idle circulating fans and steam will be shut off to cool the coils prior to shutting down circulating fans. Fire hazards associated with fan belts, fan bearings, lubricants and static are being eliminated. Steam coils are being washed on a routine basis to eliminate polymer buildup as the fire hazard increases significantly with steam temperatures. Temperatures will be regulated so that temperature of metal coils will not exceed 180°C. Tests are continuing to determine the chemical mechanism of auto-decomposition and auto-ignition of polymer.

CASE HISTORY NO. 1031

HCN Sampling Fatality

Description: A serious accident, causing the death of a sampler's assistant, occurred when a sample of hydrocyanic acid was being obtained. The draw-off point was the bottom end of a narrow bore pipe, normally closed by two valves as a precaution against leakage. Because of the extremely toxic nature of hydrocyanic acid, the pipe valves were within a closed box, having a sliding front, and to which exhaust draught was applied ty a water ejector. The assistant prepared to take a sample by putting on a compressed air breathing apparatus, connected to a nearby permanent supply. He then took the sample bottle to the sampling point and inserted it after opening the sliding door. He put in the sample bottle with his left hand and opened the lower valve with his right hand. The jet of liquid which came out was unexpected or misdirected and splashing occurred. He removed his breathing apparatus, ran to a nearby shower and operated this himself, then went to give the alarm. As neither the sampler nor his assistant was at this stage wearing breathing apparatus, both were quickly overcome by the hydrocyanic acid which had continued to escape from the open valve.

Cause: The ensuing investigation drew attention to a number of weaknesses in procedure, among them the following:

(a) The assistant was comparatively inexperienced and should not have been allowed to take the sample himself until he had gained more experience.

(b) His colleague was not in the best position to give assistance, nor did he have breathing apparatus readily available. Independent breathing apparatus, which allows more freedom of action, would have been preferable.

(c) The top valve was being left permanently open. This was a clear case where the volume of liquid that could be drawn should have been automatically limited to the amount desired.

(d) It was the practice to obtain 400 cc. at a time, whereas 125 cc. would have sufficed.

(British Chemical Industry Safety Council) Quarterly Safety Summary – July/Sept. 1964.

CASE HISTORY NO. 1032

Removing Material from Screw Conveyor While in Motion

Description: An operator was in the process of cleaning resin cake from a centrifuge basket. As the cake was broken up, pieces dropped into a hopper directly below the basket. At the bottom of the hopper, a horizontal screw feeder carried the pieces in a counter-clockwise direction to a vertical screw feeder.

The employee noticed a rubber cap over an inspection port at the end of the horizontal screw feeder pulsating up and down. He removed the rubber cap and saw a piece of cake protruding from the inspection port. As he grasped the piece of cake with his left hand, another piece came through the screw, jerking his fingers downward into the path of two steel paddles. One of the paddles caused the above mentioned injuries when his fingers were caught between the paddle and the screw feeder housing at the base of the inspection port.

His injuries consisted of partial amputation of the middle and ring fingers of the left hand and compound fracture of the index finger.

Preventive Measures:

1. A permanent Plexiglass cover has been installed over the inspection port at the end of the horizontal screw feeder.

2. A bar has been installed over an access door in the front of the hopper below the centrifuge basket.

3. A limit switch operated by the centrifuge basket door hinge has been installed to interrupt power to the screw feeder drive motor when the door is opened.

CASE HISTORY NO. 1033

Tank Incident--Nitrogen Introduced Instead of Air

Description: The removal of a side entering agitator from the MOR wash water hold tank was necessary in order to make repairs to the shaft seal. The propeller had to be removed from inside the tank before the unit could be pulled. The tank is located outside the west wall of Building 91 with a manway adjacent to the second level exit platform. The tank dimensions are 11 ft. straight side x 8 ft. 6 in. diameter. The required work was undertaken by the plant construction group in conjunction with a changeover for a defoamer run in the MOR equipment. The tank had been previously cleaned by boiling with Santomerse, boiling with Safety-Solv, and rinsing.

The maintenance foreman in charge of the work initiated a tank entry permit (work permit) at about 11:00 a.m. after checking the tank with an explosimeter and getting a safe reading. He noted under the "Protective Equipment" heading that safety glasses and a wrist harness were required. He took the permit to the Building 91 production foreman, who approved it after noting under "Special Precautions" that air was to be bled into the tank during the time that a man was inside. The Building 91 head operator then signed the permit. The maintenance foreman then gave the permit to the men who were to perform the work. He pointed out the air bleed requirement and left the immediate area to attend to other matters.

One of the men obtained a length of new rubber hose from the storeroom to use in providing the air purge and returned to the building. No one was readily available who could show him where to tie into an air supply so he took it upon himself to find a convenient source. He chose a 1/2 in. valved outlet on what he thought was the plant air header, connected the hose, put the other end into the tank, opened the valve and began to purge at about 11:45 a.m. In reality, he had unknowingly tied into a nitrogen header. The men left to perform a variety of activities which included eating lunch and having a tank ladder made up.

At about 1:45 p.m. the men returned to the job site and, with the nitrogen purge still on, one entered the tank with the other outside the manway. He entered without wearing a harness of any type. The man outside asked him if he wanted a wrist harness as he climbed down the ladder. He refused, stating he would only be a minute. (A wrist harness had been procured and was at the job site.) The man reached the bottom of the tank, took a crescent wrench from his belt and started for the agitator. At this time, his vision began to "go black" and he felt dizzy. He immediately came back up the ladder and managed to get his head and shoulders through the manway at which point the man outside helped him the rest of the way out. Total time in the tank is estimated at considerably less than one minute. The exposed man partially recovered upon reaching fresh air but some dizziness persisted. He reported to the dispensary at 2:20 p.m. where he was given oxygen and recovered completely.

Contributing Factors and Observations:

1. The exposed man did not wear a wrist harness upon entering the tank in direct violation of tank entry procedure and the specific instructions on the work permit issued for the job.

2. The time lapse between issuance of permit and actual entry was excessive.

3. Oxygen content in the tank was not determined at any time, not even at the time

work was eventually completed after this incident.

4. Had oxygen content been determined before approving permit as is sometimes done, this incident would have still occurred.

5. Advisability of using plant air to provide safe breathing atmosphere is questionable due to possibility of contamination.

6. Pipe lines are not identified.

7. Availability of self-contained breathing unit for emergency use was not specifically checked before entry.

8. There was no deviation from normal practice with respect to preparations and testing before issuing or approving work permit; it can therefore be concluded that normal practice is not adequate.

9. Two process lines tied into tank were not blanked off.

10. Tank was well cleaned.

Cause: Inadequate tank entry procedure.

Preventive Measures:

1. The following items should be made part of revision to the entry procedure now being prepared:

   a. Make tests for explosive mixture, oxygen content and suspected toxic contaminants mandatory for all tank entries.
   b. Limit time lapse between testing and actual entry; provide for continuous or periodic testing during and after entry.
   c. Strengthen rule on use of safety harness.

2. Redesign work permit to serve as a check list for items required by revised entry procedure.

3. Prohibit use of plant compressed air for providing breathing atmosphere in vessels and maintain an adequate number of Lamb air movers or similar devices for this purpose.

4. Design "Tank Entry Kit" to include at least the following items:

   a. Wrist harnesses and extra rope
   b. Explosimeter
   c. Oxygen analyzer
   d. Gas detector
   e. Self-contained breathing apparatus
   f. Communications device
   g. Entry procedure in outline form.

5. Provide training for appropriate members of supervision on all aspects of the new tank entry procedure.

CASE HISTORY NO. 1034

Laboratory Fraction Collector Explosion

Description: This accident is similar in many respects to Case History No. 592. A commercial laboratory column chromatography apparatus was being used to collect automatically fractions from a column. The developing solvent was cyclohexane, which contained a small amount of ethyl acetate. The system had been in operation overnight, and 2,500 ml. of the solvent had been collected, leaving approximately 200 ml. in the reservoir at 8:30 a.m. when two explosions occurred. Fortunately, no one was in the laboratory. People in rooms 60 feet across the courtyard from the laboratory reported seeing the room enveloped in a ball of flame which quickly subsided. A staff member from an office connected to the laboratory quickly extinguished several small remaining fires with a carbon dioxide extinguisher. Only a small amount of glassware (the chromatographic assembly) was broken. Glass shrapnel from the solvent reservoir was scattered throughout the laboratory. Other damage was slight.

Cause: As in Case History No. 592, the explosion was attributed to the ignition of flammable vapors by a spark from the electrical controls on the sampling device. The evidence in this case, however, did not indicate any likelihood of solvent overflow or spillage in the apparatus, but rather that solvent vapor accumulated to an explosion level in the enclosed portion of the fraction collector and an explosion was set off by a spark from the open electrical equipment. The second explosion presumably was that of the solvent reservoir.

Preventive Measures: All chromatographic operations using automatic fraction collection in conjunction with flammable solvents were immediately suspended until corrective measures had been taken. Although a small outlet through the wall of the fraction collector base had been provided by the manufacturer to remove solvent fumes, this seemed inadequate. An exhaust system was devised using a small squirrel cage blower driven by a shaded pole motor. Solvent vapor is vented into the hood by means of a flexible hose attached to the outlet of the blower. One-inch holes were cut through the walls of the collector box at locations which would allow a sweep of air through otherwise dead spaces and across open electrical switches. For efficient air flow, the metal dust cover which protects the collecting tubes should be in place. This equipment modification serves to remove not only flammable vapors, but also nonflammable though toxic vapors.

CASE HISTORY NO. 1035

Explosion While Introducing Chlorine into Vaporizer

Description: The injured was working in the building that houses the chlorine vaporizer. He was introducing chlorine into the vaporizer. Assisting him was the First Assistant, and a new employee who was currently undergoing training. As the chlorine was being inducted into the vaporizer, the inlet line in the top ruptured violently.

The chlorination procedure consists of routing 20 lbs. of chlorine from a chlorine cylinder-within-a-cylinder type with the chlorine injected into the inner section. The annulus space between the inner and outer cylinders contains a steam coil (15 psig steam) immersed in continuous flowing water for vaporizing purposes. During vaporization the chlorine pressure normally reaches a maximum of 100 psig. The chlorine vapor is pressured into the Reactor catalyst bed using nitrogen, then the complete system is purged with nitrogen. At the time of the inlet rupture, chlorine was being introduced into the vaporizer. The chlorine cylinder had been used for previous chlorinations and was nearing depletion. A weight measurement taken after the rupture showed 13.5 lbs. of chlorine had been removed from the chlorine cylinder. Water had been opened to the vaporizer but the steam to the coil had not been commissioned. Seconds before the rupture it was noted that the chlorine pressure was 60 psig.

When the rupture occurred the injured was in a kneeling position on the floor. He was adjusting the flow valve in the inlet line which is located just above the floor. At the same time, the First Assistant was standing close to the injured with his back at a 45° angle to the vaporizer, but with his left side closest to it. He was checking the balance of the scales and the new employee was standing close to the west doorway observing the procedure.

When the inlet ruptured, a part of the elbow in the small section of the line struck the First Assistant on the inside of his right arm just under the arm pit, to inflict a slight laceration and a bruise. The fragmentation after striking the arm caromed off and entered the right side of his coveralls to travel across his chest and emerge out at the front of his coveralls. This action caused him to fall to the floor, he then crawled out through the west door.

The injured, who was kneeling at the time, suffered a ringing sensation in his ears, as did the other two men. This sensation lasted for more than 48 hours. A peculiar aspect of the incident was that all three persons indicated they observed no odor or effect from escaping chlorine.

Cause: Immediately following the accident, a sample of the pipe fragment, along with samples of black deposits which were ejected when the line ruptured, were analyzed and the following results noted:

1. A metallurgical examination indicated that the physical condition of the pipe would not account for the rupture.

2. Analyses of the pipe fragment and ejected vaporizer deposits were as follows:

   a. Metal Fragment – inside coated with Ferric Oxide (normal corrosion product)
      - some organic material
      - some carbon.
   b. Black Solid Deposit Ejected -
      - carbon - finely divided - 20%
      - organic material - polymer of some sort - long chain - 50%
      - water plus HCL Ferric Chloride - 30%
   c. Black Liquid Deposit Ejected - Xylene plus Finely suspended carbon.

3. On the basis of these analyses, it was concluded that the rupture was the result of a spontaneous reaction between chlorine and hydrocarbon. This reaction, which does not require the presence of oxygen, is accompanied by a rapid rise in temperature and pressure. In this reaction carbon is formed similar to the deposit found after the rupture. The possibility also exists that some hydrogen could have been present which reacts violently with chlorine to give a temperature and pressure rise. There was no evidence of leakage from the water/steam side of the vaporizer to the chlorine side under pressure testing.

4. A possible reason for the absence of free chlorine could be that it was all consumed in the chemical reaction.

Preventive Measures: In order to obtain a mixture of hydrocarbon or hydrogen and chlorine in the vaporizer it is necessary to have a leak back from the reactors. At present the chlorine vent and purge lines tie into the reactor vent system, and although it would be necessary to have leakage through several valves, the possibility exists. To eliminate this possibility, the chlorination vent and purge lines are to be routed separately to the vent scrubber drum.

At present after chlorination is completed, the vaporization and injection system is purged with nitrogen and then bottled up by closing valves. It is recommended that, in the future, this system be blocked off from the reactors after each chlorination by blanking. Also the system will be purged with nitrogen before and after each chlorination.

CASE HISTORY NO. 1036

Phthalic Anhydride Tank Overflows

Description: At approximately 12:15 a.m., a phthalic department operator started the pump to transfer crude phthalic from the M8A tank to the crude storage tank. Approximately 15 minutes later, the crude storage tank was observed to be overflowing. The chief operator and the operator immediately shut down the pump and closed the valve on the M8A tank.

After the flow of phthalic stopped, the chief operator returned to the control room to arrange for control and clean up of the spill. The operator promptly climbed the vertical ladder to the top of the crude storage tank. As he approached the gauge hatch on top of the tank, molten phthalic erupted from the gauge hatch and struck the operator, covering his left arm and chest and both legs from the waist down.

The injured operator descended the 24 ft. vertical ladder by himself and proceeded to the first aid room, advising the boiler operator to notify the chief operator of what had happened.

Following first aid treatment, the injured was transferred to the hospital where he was released after treatment in the emergency room.

Cause: The cause of the crude hold tank running over was improper procedure on the part of the injured employee, who did not gauge the tank outage prior to pumping into the tank.

The reason the injured employee climbed to the top of the tank which had just run over was evidently emotional to determine the extent of damage he had caused. He stated he had no reason to go on the tank, and it was not necessary from an operational standpoint.

Why the molten phthalic erupted from the gauge hatch after all pumping had ceased is not known for certain. It is believed that inert gas purge line on the tank became plugged due to liquid phthalic entering it due to the high level. This could have caused the inert gas pressure to build to 60 psig. If the pluggage in the line was then suddenly released, 1 - 2 cu. ft. of gas would have been released below the liquid level near the gauge hatch, causing the liquid to erupt through the hatch.

The level indicator on the crude storage tank was not working properly but did not contribute to the accident since procedures call for the tank to be gauged.

Preventive Measures:

1. All employees to be reinstructed to avoid unnecessary exposure to hazards such as in this case. Case to be reviewed with all employees.

2. All operating procedures on transferring of materials be reviewed and revised where necessary by department supervision. Procedures then to be reviewed with all operating personnel.

3. a. All departments to review performance of tank level indicators and
   b. Maintenance to investigate means of improving reliability of the level gauge on the crude tank.

4. Expedite completion of a secondary escape platform from the top of the crude tank. (This was partially completed when the accident occurred. It would not have prevented injury in this particular case, but may be of value in the future.)

CASE HISTORY NO. 1037

Laboratory Accident

Description: Employee had picked up a one-gallon glass bottle containing a solution of concentrated sulfuric acid and potassium dichromate from which she poured a small quantity to clean laboratory glassware. As she was replacing the bottle on the shelf, the bottom of the bottle fell out, and the acid solution splashed over the lower part of her legs.

Cause:

1. Failure of the glass container, possibly due to improper mixing of the solution.

2. Injury might have been avoided if the bottle of solution were stored and transported in a proper container.

Preventive Measures:

1. The bottle will be kept in a protective container while it is being transported or stored. It will be taken out of container only when the solution is being poured over the laboratory glassware.

2. Dilute, instead of concentrated sulfuric acid, will be used in the future.

3. The bottles used for acid cleaning solutions will be protective-coated on the lower section.

CASE HISTORY NO. 1038

Arm Caught in Belt Conveyor

Description: An operator found that the belt conveyor which carries sodium sulfate from the filter to the dryer feed chute had stopped. Failure believed due to slack in belt which developed after belt had been removed and repaired during afternoon prior to date of accident. Belt had been reinstalled about 12-15 hours prior to time of accident and had not been adjusted. Operator tried to start the conveyor at the base, but failed. He went upstairs to the dryer room (separate room for rotary kiln) where the drive mechanism is located. At this end of the conveyor, the discharge and roll-over end, there is a smooth steel power driven pulley. The canvas conveyor belt travels around this pulley. The pulley was turning, but was slipping under the belt. The operator believed that by throwing a handful of sodium sulfate on the pulley, it would create enough friction to start the belt. (It has been learned that the belt had stopped 3 or 4 times during the shift and that the operator had started it in this manner.) He was wearing a leather palm gauntlet type glove. In throwing the sulfate on the pulley, the operator reached behind the pulley and under the belt with his right hand. As he did so, the cuff of his glove was caught between the pulley and the belt. The fastened cuff caused enough friction to start the belt moving. The operator's forearm was pulled into the nip point between the pulley and the belt. This stopped the belt, but the pulley continued to turn. He stopped the pulley by jamming a lead hammer into the drive sprocket. He still could not free his arm, however, and due to the loud noise caused by the knockers on the dryer drum, he could not make himself heard by his fellow workmen. After an estimated 30 minutes, he was able to cut the conveyor belt with his pocket knife and free himself. He then walked to the operating floor from where fellow employees took him to the Medical Department on a stretcher wagon. The accident resulted in a fracture of the ulna midway between hand and elbow, severe laceration and extensive damage to muscles; some muscle excised. The employee will suffer some loss of function of right arm and right hand.

Cause:

1. Using equipment unsafely – attempting to start defective belt conveyor and failure to call mechanic to repair conveyor.
2. Unguarded nip points.

Preventive Measures:

1. Operators instructed not to attempt to start defective conveyor belt, but to call mechanic to make necessary repair.
2. Instructional signs to be erected.
3. Emergency work order issued for installation of expanded metal guards to guard pulley nip points at each end of belt and belt roller pinch points on sides.

CASE HISTORY NO. 1039

Receives Burns While Conducting Fire Drill

Description: A fire department supervisor was drilling three firemen on pit fires at the plant's training grounds. One fire had been extinguished with foam, and the pumper had been changed over to water for the second drill. The supervisor then prepared the torch for relighting. He was using a flammable liquids mixture, poured from an open five-gallon bucket, to saturate the torch. As the mixture was poured over the torch, a flash occurred, igniting the employee's trousers. He received burns to both legs, arms and hands.

Preventive Measures:

1. Fire drills have been stopped until a thorough study has been made of the situation.
2. A hazards check list will be developed on fire drills.
3. Protective clothing and equipment will be required at fire drills.
4. A study will be made on fire-retardant clothing.
5. A safer torch will be used in the future.

CASE HISTORY NO. 1040

Failed to Shut Off Power Before Checking Driver Belt

Description: A machinist was engaged in cutting a steel rod on a power hack saw. He pushed the start button and the machine began cutting in low speed. The machine was then stopped with the stop button without releasing the tension on the blade. When the transmission was placed in high speed, an attempt was made to restart the machine by pushing the start button. The machine failed to start because the cutting blade was still under 200 pounds feed pressure.

The employee then reached behind the drive belt guard and grasped the belts to check and see if they were free. The movement of belt and the combination of the motor force caused the machine to start. The employee's hand was caught between the belt and belt guard. His injuries consisted of abrasive lacerations of the web of thumb, index and ring fingers and severe abrasive lacerations of the middle finger, left hand.

Preventive Measures: 1. All current operating procedures of the machine shop will be checked against manufacturer's instructions and a retraining program of shop personnel instituted.

2. All plant personnel will be reinstructed on safety measures relating to belt-driven equipment.

CASE HISTORY NO. 1041

Chlorine Cylinder Plug Defective

Description: While an employee and his foreman were making a routine check at a Ranney Well area, they detected a strong odor of chlorine, which was coming from a chlorine cylinder shed. The shed housed two one-ton containers of chlorine, which were connected up to the Ranney Well. Employee put on a canister type gas mask and was attempting to lift the storage shed hatch cover to find the source of the leak, when he developed respiratory distress. He was hospitalized.

Cause: Fusible plug in one of the chlorine cylinders was defective and leaking. The employee should have used self-contained breathing equipment instead of a gas mask.

Preventive Measures: Henceforth, chlorine leaks will be taken care of by the emergency crew of the supplier. Self-contained breathing equipment will be used when it is necessary to enter hazardous areas.

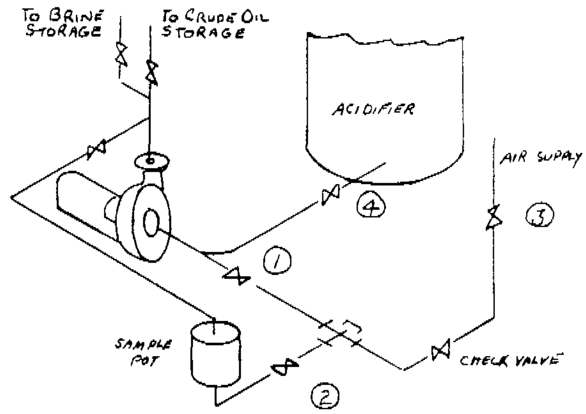
CASE HISTORY NO. 1042

Pumping Operation

Description: Employee pumped out the brine layer from an acidifier containing brine and cresol product. During the pumping operation he collected a drip sample in a sampling pot in order to identify the product layer from the brine. After he finished pumping the brine, and product appeared in the sampling pot, he diverted the flow from the acidifier to the crude product storage tank. When the acidifier was pumped empty, he closed the outlet valve (No. 4 – see sketch), and opened valves No. 1 and No. 2, to drain the sampling pot. When he opened valve No. 3 in an air line to blow out the product lines to storage, cresol and brine splashed in his face from the sampling pot.

Cause: Employee failed to close sampling pot outlet valve (No. 2 – see sketch) before attempting to blow the product line clear.

Preventive Measures: The sampling pot has been eliminated, and the layer separations are observed through a sight blass.



CASE HISTORY NO. 1043

How Safe Is the Empty Reagent Bottle?

Description: Most laboratory technicians take the safety precaution of working with and handling only prescribed laboratory glassware, equipment, etc., which is considered to be safe and adequate for the intended purpose. However, safety does not stop with the using of the right equipment as a chemist at this Arsenal learned through an unfortunate mishap.

A reassigned chemist was performing the routine chore of dusting the reagent bottles he found stored on the chemical shelf of his new worksite. He removed the ground glass stopper of an empty reagent (250 ml) bottle which had previously held ether, $(C_2H_5)_2O$. When he replaced the stopper, there was a sudden explosion which completely disintegrated the stopper, neck and shoulder of the bottle. Fortunately, no injuries or property damage (other than the bottle) resulted.

Cause: After careful investigation, it was learned that the explosion was caused by a residue of unstable peroxides and/or oxides of ether, which had formed in the ground glass portion of the bottle. Ignition was initiated by the friction heat generated when inserting the stopper.

Preventive Measures: All laboratory personnel should be constantly aware of the danger of allowing chemicals and empty chemical containers to accumulate and to remain on shelves indefinitely. Equipment and apparatus should be thoroughly cleaned after completion of work.

U.S. Atomic Energy Commission Case History.

CASE HISTORY NO. 1044

Plastic Tubing Rupture Releases SO_2-- Two Men Injured

Description: Two laboratory employees were injured recently when a length of plastic tubing ruptured and sprayed the men about the face with corrosive sulfur dioxide.

This accident resulted in some temporary eye and lung damage. One employee was hospitalized for three days; the other was taken to a hospital for overnight observation. The latter employee had been wearing safety glasses, which undoubtedly saved his eyes from more serious injury. Two other employees in the area at the time inhaled enough SO_2 fumes to require local treatment.

This incident took place during the testing of a gas scrubber system. Sulfur dioxide was being introduced into the system as a contaminant gas through a 1/2 inch plastic tube. The rupture occurred while the employees manipulated valves between the SO_2 cylinder and the vaporizer. Maximum pressure on the system at the time of the accident was approximately 35 psi (the vapor pressure of SO_2 at room temperature). The action of SO_2 on the plastic tubing apparently weakened it and resulted in the rupture.

Cause: Although fresh plastic tubing (of the type involved) will withstand pressures up to 100 psi, it is not considered an adequate material for pressure systems. Such tubing may be weakened by a variety of chemicals and physical conditions. This weakening is unpredictable and may result in a rupture at low pressures.

The accident described above is typical of a number that have occurred recently in AEC activities and in other industrial or laboratory operations outside of the Commission.

This problem has become more prominent with the growing misuse of plastic and glass for moving hazardous liquids, solids and gases from one place to another either by gravity flow or under pressure.

Another facet of the problem concerns the method of fastening and couplings used in attaching tubing or piping to vessels, cylinders, or apparatus. Too frequently the tubing is slipped onto a nozzle without any fastenings or couplings, and sometimes couplings are of a type that can work loose and separate. These conditions also set the stage for an unplanned release of a hazardous material.

Plastic tubing is manufactured from a wide variety of different compounds and is resistant to chemical and temperature effects in varying degrees. Most have one common weakness – they soften and/or melt at elevated temperatures and some will burn when subjected to flame. The weakness of glass tubing and piping is that it will fracture when subjected to impact, unusual strain, or sudden extreme temperature change.

We do not wish to imply that such materials should never be used – but – these accidents suggest that, before they are used, a hazard review be made to determine the results of a possible failure and whether or not released material can be confined within an enclosure or system where it cannot cause injury, unplanned damage, fire, or explosion.

One of the most common hazards found in a number of laboratories is plastic and other types of tubing connected to the nozzle on a cylinder of highly toxic, flammable, or explosive gas without a clamp or with an inadequate device for securing the tubing to the nozzle. In the majority of such cases, the unsafe practice causes no trouble but, occasionally, a serious accident results when the tubing either slips off or is blown off, releasing the hazardous material.

Preventive Measures: Here are a few questions for determining whether an assembly of plastic or glass tubing might be safe to use:

1. Is the tubing part of an assembly to be used in an enclosure where a rupture will not affect personnel or cause a serious accident?
2. What are the temperature and pressure limits of the plastic or glass tubing to be used? If glass, what impact hazards prevail?
3. Is the tubing chemically compatible with the material to be run through it?
4. Is the proposed location for its use such that it could be pulled loose or broken by passing traffic (people, carts, etc.)?
5. Is it to be used on a bench or location where flames are also used?
6. Would it be safer to use metallic tubing?
7. Will the method of securing the tubing hold under conditions of pressure and/or temperatures available or anticipated?

These questions are just a few suggested by the accidents that have occurred.

U.S. Atomic Energy Commission Case History.

CASE HISTORY NO. 1045

Explosion--Experimental Fluorination

Description: An experimental fluorination was being conducted in a 304 stainless steel one liter round-bottom flask. The flask was fitted with a paddle-type agitator, a straight-tube reflux condenser, a thermocouple well and a gas inlet tube. The system was placed in a laboratory hood and protected by a 1/4-inch plastic shield. After cooling the reactor to -50°C and the condenser cooling medium to -70°C., introduction of the fluorination mixture was commenced. Progress of the reaction was checked every half hour by a technician trained in handling experimental fluorinations. The addition of about 160 g. of fluorine proceeded over a 10-hour period uneventfully. At the end of this period there was a sudden explosion without any warning as the technician reached into the hood to test for excess fluorine at the top of the condenser tube. Although his hand was protected by gloves and the starch-iodide test paper was held with a 10-inch forceps, the force of the explosion caused a severe hand injury. Subsequent examinations of the remnants of the apparatus by explosives experts indicated that the explosion occurred in the vapor phase.

Cause: A new route to the preparation of perfluoropropyl hypofluorite was being investigated. The reaction was expected to proceed through cesium perfluoropropoxide. This had been prepared the previous day, the apparatus cleared with argon, blanketed with nitrogen and cooled. The fluorination mixture was approximately 50/50 fluorine and nitrogen. Literature studies had indicated that the reactions could be handled without undue hazard, but quantities were kept low and the apparatus was shielded. Investigations subsequent to the explosion indicated the possibility of a small amount of water being introduced due to the low temperature. Water could be expected to convert some of the perfluoropropionyl fluoride (used in primary reaction) to the propionic acid, a precursor for an acyl hypofluorite. (It is well known that perfluoroacyl hypofluorites are explosive.)

From the structures that may have been present in the reaction mixture it is possible that the following potentially-explosive types of compounds could have been formed: bis (perfluoroalkyl) peroxides, bis (perfluoroacyl) peroxides and perfluoroacyl peresters. The explosion may have been initiated by the grinding effect of the agitator paddle on nearly dry solids in the flask, following extended sweeping with nitrogen.

Preventive Measures: Scouting experiments involving fluorine should be kept to 25 grams maximum, and should be conducted in blast-resistant hoods. Manipulations should be done with extension devices from the outside of the barricade. Fluorinations on a larger scale than 25 g. should be carried out by remote control behind an appropriate steel barricade in buildings constructed for this type work, outside the laboratory building.

CASE HISTORY NO. 1046

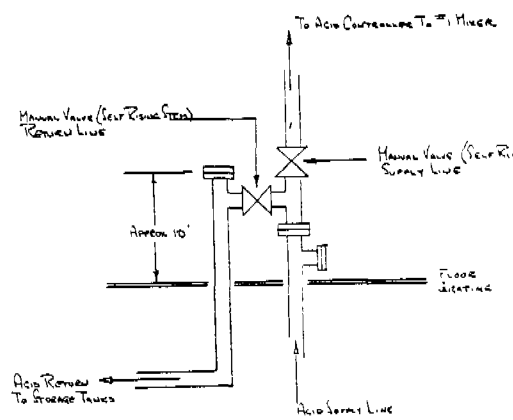
Valve in Acid Line

Description: Two mechanics had been assigned to the job of replacing the existing phosphoric acid return line between the #1 mixer in the S.T.P. Department and the acid storage tanks. They had already completed the necessary shop fabrication and field welding and were ready to make the final connection at the manual valve on the return line. (See sketch) On the day of the incident, the mechanics involved did the following:

1. Told the production foreman that they were going to break into this acid line and make the final connection.

2. Asked the production foreman to have the valves on this return line at the storage tanks opened by the acid operator.

3. They then went upstairs to the job site and attempted to close the valve on the acid return line (see sketch). They found this valve to be extremely hard to operate. After cleaning the valve with steam, they attempted to close the valve by using a pair of channel-lock pliers. They succeeded in closing the valve part way and although the rising steam was escaping through the handle, they assumed the valve was closed and proceeded to loosen the bolts in the blind flange just after and above the return valve (see sketch). When the fourth bolt was loosened, acid under pump pressure sprayed onto both mechanics around their ankles. The return line valve was then completely closed by a production operator using a 14 inch pipe wrench.



Note: Neither mechanic was wearing the prescribed eye protection for performing this work as outlined in their departmental safety rules.

Cause: 1. Improper method in performing this work was used by these mechanics. Although there were several possible ways of relieving and determining whether or not there was pressure on this line before disconnecting, nothing was done.

2. Improper attitude was a cause, because the time necessary to perform the work was thought to be more important than taking the necessary safety precautions.

3. The defective valve was a contributory cause, because if the valve functioned properly the incident would not have occurred.

Preventive Measures: a. Repair or replace defective valve.

b. Add vent on return line for future maintenance work.

c. Review incident in all departments with all plant personnel. Points to review:

1. Safety attitude
2. Hazards of handling phosphoric acid.

d. Review maintenance department safety rules.

CASE HISTORY NO. 1047

Laboratory--Flask Handling

Description: A lab analyst was attempting to remove the stopper from a 50 ml round bottom flask containing 1 ml of lactic acid and 3 ml of 30% caustic which had been immersed in liquid nitrogen at -320°F. A violent implosion of the flask resulted while it was still in her hands. Fortunately, she was not injured, but a serious injury could have resulted.

The stoppered flask had been exposed to an ambient temperature of 75°F. prior to being placed in the cold bath. The change in temperature (approximately 400°F.) caused an intense vacuum within the stoppered flask, and the implosion resulted.

Cause: Improper procedure: Flask was tightly stoppered when exposed to a large reduction in temperature.

Preventive Measures: The procedure of removing the stopper before immersing flask in liquid nitrogen baths will be emphasized and followed. Also, analysts will be reminded of the importance of using their face shields and asbestos gloves when handling any material which is being exposed to radical changes in temperature.

CASE HISTORY NO. 1048

Explosion--Silver Oxide

Description: A chemist attempted to dissolve 3 moles of silver oxide, prepared 24 hours earlier and held in a sealed flask as a water slurry, by addition of ammonium hydroxide. Dissolution did not occur as expected and addition of hydroxide was continued, necessitating transfer of the slurry from a one-liter flask to a five-liter stainless steel can. As manual stirring continued a muffled explosion sufficiently violent to distort the bottom of the can occurred, blowing the slurry throughout the room and spattering the four workers present. The wearing of safety glasses by all of these employees and of rubber gloves by the chemist, plus prompt use of the nearby safety shower and eye-wash fountain, avoided a major injury, although all suffered chemical burns. Continued "pops" and "bangs" from the area indicated a persistent hazard, and personnel experienced with explosives were called upon for assistance. Spraying with slightly acid sodium chloride solution from behind a heavy steel shield successfully decontaminated the room and equipment by converting the silver oxide to chloride.

Cause: Although it is known that certain silver complexes present explosion hazards, the reaction which here occurred is not understood. Similar procedures, without the 24 hour holding period, had been carried out without incident. No formation of hazardous compounds was expected, and holding in water was regarded as extra protection. Possible reactions leading to explosive compounds are formation of silver fulminate from reaction of silver oxide with carbon dioxide from the air, catalytic action of the metal can, or silver imide formation.

Preventive Measures: 1. Do not attempt similar non-standard silver compound reactions until better understanding has been achieved and/or better protective arrangements established.

2. Broadly review the literature on hazardous silver compounds, and supplement with experiments if feasible, to establish better guides for undertaking reactions in this field. Make sure that the technical staff is fully informed of the conclusions.

3. When reacting more than one mole of ammoniacal silver nitrate use a metal con-

tainer, and wear face mask, rubber gloves and rubber apron. Do not hold such a solution more than one hour.

Editor's Note: Additional preventive measures are needed: Use only glass apparatus in such work. Try at all cost to limit quantities to less than one gram mole. A range of 1 - 10 grams is suggested.

CASE HISTORY NO. 1049

Glass Ampoule Explodes

Description: An employee placed a 35 ml glass ampoule in a dry ice bath and filled it three quarters full with an organic bromide, an amine and an alcohol. He then sealed the ampoule and removed it from the dry ice bath. The employee ran water over the ampoule in three ten-second intervals. Returning the ampoule to the hood from the sink, the employee noticed the reaction starting to boil. As he was reaching to place the ampoule in a steel beaker, it exploded, cutting both hands.

Cause: Running tap water over an unshielded glass ampoule.

Preventive Measures: The department will prepare written instructions for safe handling of pressure reactions in both glass and metal equipment. These written instructions will be used in training employees and will include:

a. Sealed reactions of any nature will be reviewed by the supervisor prior to experimentation.

b. A metal type shield to contain the glass tube.

c. Specific shielded area with necessary equipment to conduct pressure reactions.

d. Fluid sand bath will be used to warm reactions.

CASE HISTORY NO. 1050

Failed to Properly Set Valve

Description: A sodium fluoride mix was being prepared. The bulk of the required soda ash had been added to the SSF slurry and steam had been turned on to raise the temperature. A laboratory check required an additional 3 inches of soda ash. The operator set his valves and started the pump to accomplish the job. A 3 inch gate valve in the soda ash line is normally used to regulate the rate of addition of soda ash to the mix. This valve is normally 1-1/2 turns open. It is believed the addition was made with the valve in a wide open position. When the soda ash entered the mix tank, it erupted violently, spewing the contents out through the openings in the top of the tank. Some of the hot liquor (95°C) contacted the operator causing first and second degree burns on his entire back from waist to neck, arms, hands and area of both ankles.

Preventive Measures:

1. An orifice plate has been installed on the discharge side of the 3 inch throttling valve to regulate the rate of flow of the soda ash solution.

2. The details of the accident were reviewed with other department personnel.

CASE HISTORY NO. 1051

Gasket Failure

Description: An employee noticed steam leaking at a lower corner of a door on an autoclave. As he attempted to tighten the door, the gasket blew out and he was sprayed with steam. He received first and second degree burns of his face and body. The door was dismantled; the threads on the door post were found to be corroded. The brass screw box was stripped. The corroded threads and the stripped brass screw box permitted the door to move out, but not open, allowing steam to escape with force enough to rupture the gasket.

Preventive Measures:

1. Autoclaves will be set up on the preventive maintenance schedule.

2. Autoclaves with a history of continuous leaking at doors will be dismantled and checked.

CASE HISTORY NO. 1052

Fork Truck Incident

Description: A welder had been welding a staple bale conveyor and after completing the job was being lowered to the floor approximately 8 feet below on a pallet placed on the forks of a fork truck. The pallet was not equipped with hand rails or clamps to hold it on the fork. The hoist apparently hung on the second conveyor momentarily and suddenly dropped about 8 inches causing the injured to lose his balance and fall. He suffered contusion to chest and left side resulting in traumatic pleurisy. The fork truck was examined immediately after the accident and found to be in good operating condition, thus a mechanical failure of the fork truck was ruled out.

Cause: Unsafe condition — hazardous arrangement (position of fork truck in relation to conveyor and use of pallet without clamps or hand rails).

Preventive Measures: Care must be continually exercised when operating motor vehicles to maintain clearance with obstacles. All pallets used for work platforms must be equipped with hand rails.

CASE HISTORY NO. 1053

Explosion Within Glovebox Disperses Contamination

Description: Ignition by unknown sources of a methanol-air mixture led to an explosion within a glovebox line in which 17 grams of plutonium 238 were being processed. No one was injured; however, the explosion pressurized the boxes and caused a total of six gloves to be torn from the ports.

Plutonium oxide discharged from the open gloveports and spread throughout operating areas of the building. Swipe specimens (40 sq. in.) indicated loose contamination ranging up to 4×10^6 d/m. Contamination cleanup costs approximated $33,000.

All employees in the room were wearing half-mask respirators at the time of the explosion. Three of these men had completed a glove change on a box on the other side of the room just before the explosion occurred. During glovebox changes, it is standard procedure for all personnel in the room to wear respirators.

The clothing and external body surfaces of three employees were contaminated. Body surface contamination readings (using commercial alpha survey meters with 55 cm^2 windows) varied from 100 to 1,300,000 c/m. Decontamination of these individuals was effected with little difficulty. These same three men also had initial nose swipes ranging from 44 to 10,000 d/m indicating internal contamination. The three were treated with DTPA. On the basis of previous experience and an analysis of blood, fecal and urine samples, it is roughly estimated that the plutonium body burden for two of these men is less than 10% of the permissible amount and less than 50-75% of the permissible amount for the third individual.

Preventive Measures: Steps taken to prevent recurrence of similar incidents include the following actions:

1. Use of flammable solvents within gloveboxes has been prohibited.
2. A complete reevaluation is being made of the area ventilation system with respect to control of airborne plutonium.
3. Self-closing hardware will be installed on emergency exit doors. (Note: It is thought that doors left open by evacuating employees contributed to contamination spread.) A program has been initiated to reinstruct existing employees as to standard operating and emergency procedure requirements.
4. A permanent "Hazardous Chemicals Committee" has been formed to maintain a continuing review on the use of chemicals within the building.

Gloveboxes afford a commonly used means for working with hazardous materials under conditions preventing their escape to external areas. Fire and explosion constitute the most common serious threat to glovebox integrity. A Chicago Operations Office contractor is currently making an intensive study of the most effective methods for detecting and suppressing glovebox fire and explosion hazards. Results of this study will be published in the fall of 1965.

U.S. Atomic Energy Commission Case History.

CASE HISTORY NO. 1054

Inhalation of Toxic Fumes--Chemical Cartridge Respirators Prove Inadequate

Description: Two maintenance men were replacing a stainless steel flanged elbow on a tank. One man held the elbow, while the other man lay on his side replacing the flange bolts. Both men were wearing chemical cartridge respirators. In a few minutes, both men left the job area and went out to a loading dock a few feet away to "get some fresh air" because of fumes that had come through or around their masks. They alternated between the dock and work area until the job was completed. The replacement of the elbow took about 30 minutes, of which 15 or 20 minutes were spent in the work area. At the completion of the job, one man became ill and was hospitalized. It is believed that the inhalation of these fumes was sufficient to trigger an attack of a pre-existing condition for which the man was being treated.

Preventive Measures:

1. Fumes will be reduced by cleaning the equipment more thoroughly when jobs of this nature are performed.
2. Proper type of mask will be worn when performing jobs in vapor areas.

CASE HISTORY NO. 1055

Tank Rupture--Caustic Soda

Description: The top of a 150,000 gallon vented tank over half-full of caustic soda was violently ruptured around approximately one-third of its periphery, above the level of the tank contents. It is believed that an ice blockage of the vent prevented relief of the air used to blow out the caustic supply line, thereby allowing a pressure build-up.

Cause: On the day prior to the occurrence, a tank truck of 50% caustic soda was received for dilution and unloading. When the operator attempted to pump through the unloading line, he found that it was blocked with ice as a result of improper draining during the previous unloading. The ice block was cleared by pressuring and depressuring the line with 60# steam. Apparently when the length of line to the tank cleared, steam flowed into the tank and out through the 6 inch vent. The vent consists of a 180° U-bend with a 1/4 inch screened opening facing downward. An examination of the tank roof after the failure revealed a collection of ice under the vent. This leads to the conclusion that condensing steam froze out on the 1/4 inch mesh covering the vent pipe leading eventually to a complete ice blockage.

When the caustic unloading was complete, the line was flushed with water and blown with air. When the drain lines were cleared of water they were closed and an air flow was left on the line to clear any residue of water. Approximately five hours after the air was applied to the line, the tank roof seam failed. It is concluded that air pressure build-up was a consequence of ice blockage of the vent pipe.

Preventive Measures:

1. It is recommended that this tank be equipped with a new style of vent pipe which will not be susceptible to ice build-up.

2. This tank, and any other tanks which may be accidentally subjected to pressures over their design rating, should be equipped with suitable rupture discs.

3. Any vessel which is not equipped with a pressure relieving device should be blanked off before any of the connected piping or auxiliaries are subjected to pressures in excess of the vessel rating.

CASE HISTORY NO. 1056

Nitrogen Compressor Explosion

Description: A four-stage reciprocating compressor was used to recycle high-purity nitrogen gas from the low-pressure distillation column to the high-pressure distillation column of a nitrogen liquefaction facility. The Cellulube 550 lubricated compressor normally took suction at 15 psig and developed a maximum discharge pressure of 3,000 psig. The compressor was equipped with appropriate pressure relief safeguards.

Prior to the explosion, the operator noted that the third-stage safety relief valve was "blowing." The entire plant was shut down to permit the removal, inspection and replacement of the third-stage inlet and discharge valves. When restarted, the second-stage relief valve began to "blow" immediately. After again shutting down the compressor, the third-stage suction valve was "inspected for the correct direction of flow and found to be reversed." It was shortly after this error was corrected and the compressor restarted that the explosion took place. Subsequent investigation established that the third-stage suction valve had indeed been installed properly but that the discharge valve had been installed in a reversed position.

The explosion ruptured the compression jacket and projected metal fragments up to 160 feet from the building. Witnesses reported seeing a "brilliant flash" at the compressor. There were no injuries. Property damage is estimated at $16,000.

Cause: With the third-stage discharge valve in a reversed position, compression of gas within a closed volume would, theoretically, have permitted attainment, during a single cycle, of a gas temperature approximating 1310°F and a pressure of about 16,800 psig. These conditions in the presence of some oxygen from air introduced during compressor maintenance, exceeded the autoignition temperature of the compressor lubricant and resulted in an explosion.

Recommendations and Conclusions: Prior to the accident, no standard procedures were in effect to substantiate that a compressor was in operable condition following conduct of maintenance work necessitating exposure of the compressor interior to the atmosphere. To prevent recurrence of similar incidents, the investigating committee recommended:

1. Operations Test: A 20-psig, high-purity gaseous nitrogen purge line should be installed to the suction line of the nitrogen compressor. The suction and discharge valves in the first, second, and third-stage discharge blow-down valves should all be closed. With the 20-psig purge valve open, the fourth-stage discharge blow-down valve should be checked for positive flow to indicate that the compressor valves are in the correct position. Should a valve be

inadvertently installed in the reverse position, there will be no flow from the fourth-stage discharge blow down. After this test has been completed, the purge flow can be closed by a valve and the compressor made ready for startup.

2. Maintenance Test: After maintenance has been completed, the compressor fly-wheel should be turned by hand a minimum of two revolutions to be assured that no obstructions exist in the machine. All compressor discharge blow-down valves should be opened during this test.

3. A similar test procedure should be established for the air compressor. However, instrument air should be used as a purge gas in lieu of high-purity nitrogen.

4. An oxygen analyzer should be installed on the suction line from the low-pressure column to the nitrogen compressor. Should the oxygen concentration in this gas stream exceed a pre-set level, the compressor suction should be automatically valved to an independent high-purity nitrogen supply until this condition no longer exists. A pre-set level should be determined to allow for automatic operation and yet prevent an enriched oxygen stream (greater than 21%) from being pumped by this compressor.

U.S. Atomic Energy Commission Case History.

CASE HISTORY NO. 1057

No Lock-Out; Killed in Mixer

Description: Two maintenance men were replacing part of the ribbon in a ribbon mixer. The switch was left in, and energized; the mixer had been stopped by one of three start-stop buttons.

As one mechanic was completing his work inside the mixer, a workman on another floor pushed, by mistake, another of the start-stop buttons. The mixer started, killing the mechanic between the ribbon flight and the shell of the vessel.

Cause: 1. Not taking preventive measures. Switch should have been padlocked "off" and/or fuses pulled.

2. Mixer was a closed vessel and hence a tank. Tank entry rules, which include multiple lock-out, should have been followed.

Preventive Measures: 1. Enforce lock-out and tank entry rules.

2. Both operating and maintenance personnel should lock main switch and not remove their locks until they agree that it is safe to do so.

Editor's Note: 1. I would like to suggest that the padlock NOT be placed at ribbon mixer or other piece of equipment. The padlock should be placed at the starter switch box disconnect which is usually many feet from the vessel being "locked out." Shorts or grounds can and have occurred in the control circuit, bypassing the push button switch at the kettle and making it possible for the agitator to be energized.

2. After "locking out" the disconnect, the man who will be entering the vessel should push the "ON" button or switch located at the vessel. In this way he can be more certain that the correct agitator has been locked out.

CASE HISTORY NO. 1058

Chemical Spray

Description: Injured had completed a reaction involving fluorinated alcohol and phosphorous pentachloride and had distilled off the product. The residue (about 500 ML) was poured into a one liter flask, which was about 2/3 full of crushed ice, to decompose the by-product (phosphorous oxychloride) of the reaction. He stopped stirring the solution for about 30 seconds, to obtain additional ice and when he started to insert the stirring rod to continue stirring, a violent reaction occurred, throwing the solution on his head, face and eyes and right shoulder. Medical examination disclosed first and second degree burns on the forehead and cheek and minor irritation to the eyes. Wearing of safety glasses prevented more serious damage to eyes.

Preventive Measures: The bumping would not have sprayed such a broad area if a narrow-necked flask had not been used. A large beaker of ice would have prevented the spray. In future, shields will be used to protect workers in operations of this nature.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1059

"Safe" Gases Can Be Dangerous

Description: A potentially serious accident occurred during changes to a pressure controller on a nitrogen manifold.

Nitrogen is, of course, a non-hazardous gas – it makes up nearly 80% of the air we breathe – and yet too much nitrogen can create a problem by reducing the amount of oxygen if a very large quantity of nitrogen is released.

In this instance, changes were being made to a pressure controller for a reserve bank of nitrogen cylinders located in a compressor room. A new pressure tap was being provided. In the course of the work the mechanic closed the valve on the original pressure connection, not realizing that this would cause the controller to open. Full cylinder pressure of 2,000 psi was released into the 150 psi piping causing relief valves, which discharged inside the building, to open.

The mechanic left the area immediately and met another man, the "outside services operator." This operator tried to get assistance by phone but could not because of the noise of the escaping gas.

Without going into detail about the action of several persons who became involved in handling the emergency, it appears that one man, the "outside services operator" collapsed inside the building and was in the area an appreciable time.

Two men (one of them the mechanic who had been working on the system) attempted a rescue but realized they could not move the injured man and collapsed themselves just inside the door. Properly equipped emergency personnel helped these two men out of the building and then removed the injured man. All three were taken to the Medical Department. The two would-be rescuers were released almost immediately. The man who had received the maximum exposure was taken to the hospital and released after two days.

The accident points out the hazards that may be created by relief valves discharging within a building, even for a quite harmless material.

CASE HISTORY NO. 1060

Electrical Failure--HCl Release

Description: Two mechanics, wearing full acid suits with breathing air to the hood, were replacing a valve in the discharge line from the HCL separator to a scrubber. Isolation of the section of the line included reliance on an electrically-actuated, air-operated plug cock. An electrical fault, believed to be caused by snow blowing into the top vent of the substation cubicle and being melted by a small leakage current over the face of the insulator and then combining with the dust on the insulator to form a path to ground, in a load break switch in another area of the plant resulted in a complete power failure. This failure de-energized the solenoid valve controlling air to the plug cock operator, causing the valve to change from the closed to the open position. The failure of electricity also resulted in complete darkness in the building and rapid loss of plant air flow to the acid suit hoods. The opening of the plug cock allowed gas in the chloride scrubber to escape through the opening in the pipe line where the mechanics were working. One employee escaped from the area without incident; the other apparently became lost in his search for the door to the stairwell leading to the ground floor. Two rescue attempts were unsuccessful because of evidence of leakage around the face piece of the masks worn; the third attempt, about 15 minutes after the incident, was successful, but the employee died the next day at the hospital. A member of the emergency brigade assisting in the rescue apparently inhaled some HCl fumes during the brief period his mask was removed when it caught on some obstruction. He recovered after a few days in the hospital.

Cause: Although the job had been preplanned by operating supervisors in the field, it was reviewed with the maintenance foreman and the two mechanics at the semigraphic panel in the control room. The valve and piping arrangement shown by the panel for this portion of the operation was not entirely accurate. In addition, there was excessive reliance on electrically-operated equipment.

Preventive Measures: Filters are being installed on enclosed substation vents to prevent entrance of snow and reduce dust accumulation; insulators in enclosed switch gear will be cleaned annually. Equipment shutdown for maintenance will be checked visually instead of relying on diagrams or panel boards. Procedures have been revised to include a requirement that automatic valves used for isolation purposes shall be rendered inoperable in the closed position. In addition, consideration is being given to providing additional emergency lighting and a stand-by air supply, as well as locating breathing-air stations near doorways so that employees can follow their air hose to an exit.

CASE HISTORY NO. 1061

Leaking Natural Gas Follows Water Main

Description: While mechanic was in an enclosed water-meter pit to make routine readings and inspection, an explosion occurred. The source of the explosion was natural gas which had followed the water main some 50 feet from a leak in a gas main. The source of ignition has not been determined – possibilities include smoking (employee's pipe and lighter were found on the pit floor), the open contacts of the float switch on the water siphon pump, and the heat lamp which was found broken after the incident.

Preventive Measures: Standard practice for vessel entering has been revised to require gas testing before entering any size or type of vessel regardless of use or location.

CASE HISTORY NO. 1062

Using Improvised Wrench

Description: Injured was opening a drum of hexamethylene diamine at the drum melter. The drum melter heats the drums to 120°F to liquefy the contents and a slight pressure builds up inside the drum.

There was no standard bung wrench immediately available at the drum melter so he improvised and using a crescent wrench and a screw driver, he applied leverage with the screw driver. The bung suddenly loosened. This caused him to lose balance and lean over the loosened bung of the drum.

The slight pressure caused droplets of the liquid hexamethylene diamine to spew from the bung when it loosened. It splashed under the lower rim of the face shield onto the injured's face and into both eyes.

Cause: Using the improvised tool which caused him to be in the unsafe position.

Preventive Measures:

1. Standard bung wrenches are to be used for opening drums.
2. Splash guards will be installed on the bung wrenches.
3. Chemical splash proof goggles, as well as face shields, will be used when pumping hexamethylene diamine or handling caustic or acid in the demineralized water preparation area.

Editor's Note: Drums should NOT be placed in "drum melters" until AFTER the bung has been removed. At that time the operator may:

1. Place the bung on the drum top but not over the hole.
2. If vapors are too irritating:
   a) a rubber stopper with 1/8 inch or 1/4 inch hole can be inserted.
   b) drill a 1/8 inch hole in a plastic cap and place the plastic cap over the bung opening. Pressure cannot build up even if the hole becomes plugged.

CASE HISTORY NO. 1063

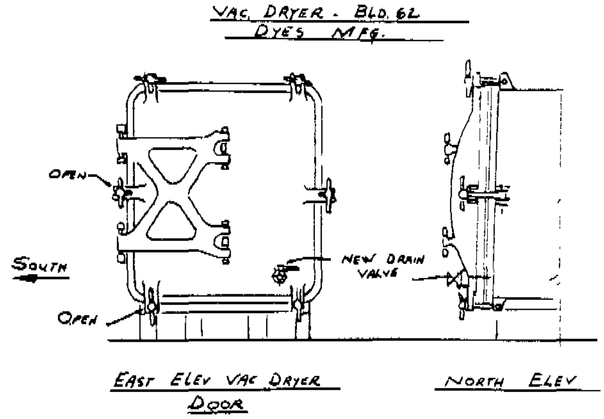
Vacuum Dryer

Description: An employee was in the process of opening a vacuum dryer which had been boiled out for repairs and was full of hot water. He loosened the middle lug on one side of the dryer door and he then proceeded to open the bottom lug on the same side. The hot water came out of the dryer very suddenly and splashed on the employee's legs and feet. (See sketch).

Cause: Employee apparently did not follow the accepted procedure of opening the bottom lugs before opening the side lugs. Opening the side lugs allowed the hot water to splash out on the employee.

Preventive Measures:

1. The doors on this and other comparable dryers in the department are being modified to provide a low level drain.
2. A Job Safety Analysis will be completed for the cleaning out of vacuum dryers.
3. A program of re-instruction on the proper method of boiling out and draining these dryers will be conducted for all personnel who work in these areas.
4. The wearing of extra protective equipment will be required for the operator whc drains these dryers in the future.



CASE HISTORY NO. 1064

Sulfides in Acid Sewer

The accident occurred recently in a large chemical plant at which operations include the production of benzyl polysulfide. Normally, liquid sodium sulfhydrate is delivered to the plant in large tank cars and transferred through completely enclosed pumping systems to a 5,000 gallon storage tank. From this tank the sulfhydrate is moved further through another closed pumping system to a mixing tank containing sodium hydroxide to form sodium sulfide solution for later use in the manufacturing process. Hydrogen sulfide is not formed at any stage of the process and has never been a problem. The sewer drains in the area where this process takes place connect with the general sewage system of the plant. Ordinarily, wastes from other processes in the plant render the sewer contents somewhat acid.

On the morning of the accident, the pump leading from the storage tank which contained

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sodium sulfhydrate to the mixing tank containing sodium hydroxide was started. When the gauge did not show adequate flow, live steam under 120 pounds pressure per square inch was applied to the pump to clear the lines. The housing of the pump broke and the adjacent pipe leading from the sulfhydrate tank promptly ruptured. Liquid sodium sulfhydrate poured onto the ground and into a nearby sewer where it immediately reacted with the acid sewage, releasing excessive amounts of hydrogen sulfide gas from several sewer openings within a radius of 150 feet. Some of the gas was spread further by natural air movement so that a faint odor of the hydrogen sulfide gas was detectable 500 feet downwind from the damaged pump.

Evacuation and rescue operations began immediately. Within a few minutes the nature and source of the exposure were recognized, and several tons of caustic were dumped into the sewer to terminate the generation of the hydrogen sulfide gas.

Toxic Effects: There were 89 people present in the contaminated area during the time the hydrogen sulfide gas was generated. Fifty-two of those present showed some evidence of hydrogen sulfide intoxication and in 12 the intoxication was severe. Two of the 12 died, probably as a result of respiratory arrest; three stopped breathing but were resuscitated; six lost consciousness initially but recovered and one individual developed pulmonary edema which responded to therapy. The clinical picture of the remaining 40 persons was considerably less severe and only mild in many.

(Courtesy of Morris Kleinfeld, M.D., New York Division of Industrial Hygiene.)

Comment by MCA: The foregoing excerpt is from Industrial Medicine and Surgery 33, 656 (Sept. 1964). Preventive measures in similar exposures would include:

1. Install permanent dike for high hazard areas.

2. If dike is impracticable, divert spills to a separate sewer or sump, free from acid wastes.

3. Before using high-pressure steam, determine the safe working pressure of all components.

CASE HISTORY NO. 1065

Trichloroethylene and Caustic

Description: Two men were seriously burned about the hands and face while working near a caustic cleaning tank in the metal heat treating department.

The caustic was in a 100 gallon, rectangular, steel tank with an open top. It was heated by direct fire and controlled at 190°F. One of the operators emptied approximately 4 gallons of clear liquid, from an unmarked pail, into the tank. There ws a sudden geyser-like reaction in the tank followed by a fire-ball. Both men had their clothing catch fire and suffered appreciable first and second degree burns about the upper torso.

Cause: The pail contained Trichloroethylene. The operator thought it was water. Trichloroethylene boils at 188°F; as this dense material sank below the surface it was rapidly converted to vapor which caused rapid eruption of the caustic. Samples of the two materials were mixed in the laboratory without any resulting fire, but the literature, including the MCA Data Sheet for Trichloroethylene, clearly states that "strong alkalies may react with Trichloroethylene to form explosive mixtures (Dichloracetylene)". The walls of the room had a coating of oily soot after the incident, the clothing of the men caught fire and their burns were of a thermal nature.

Conclusions:

1. All containers should be marked or tagged.

2. Trichloroethylene, one of the "Safety Solvents" is not a fire hazard under the usual working conditions. However Trichloroethylene and strongly alkaline solutions are used in close proximity many places. All employees should be taught that these materials must not be mixed, that the hazards are greatly increased if the caustic is heated, and that an explosive problem can exist under these conditions.

CASE HISTORY NO. 1066

Phosphine Explosion

An explosion occurred recently in an apparatus used for the routine preparation of phosphine. The apparatus consisted of a generator, in which water could be dripped on to a calcium phosphide, and two drying towers filled with calcium phosphide. A yellow/orange deposit covered the calcium phosphide in the drying towers, which were not refilled from run to run; this deposit is a well-known but ill-characterized material, believed to consist of networks of phosphorus atoms with terminal valencies satisfied by hydrogen.

The explosion occurred within a minute of filling the dry generating flask with calcium phosphide and starting to flush out the apparatus with argon. The site of the explosion was one of the drying towers, of which only the necks and a base remained afterwards. The operator received cuts and later showed very slight symptoms of phosphine poisoning, but fortunately sustained no permanent injury.

The cause is believed to have been the presence of phosphine in the drying towers at the beginning of the operation. This could have been slowly generated since the previous run, either by ingress of moisture or by desorption from or decomposition of the solid in the drying towers. When the argon flow was started, the first effect would have been to blow the air in the generating flask through the drying towers, and this evidently created the conditions for explosion. Contributory causes may have been the dry conditions (moisture inhibits phosphine-oxygen explosions) and slight external heating as a result of proximity to other apparatus (the explosive limits expand rapidly with rise in temperature). The possibility cannot be ruled out that the yellow-orange solid may also have been involved, e.g., as a catalyst, though the literature gives no indication that the solid is itself explosive.

This incident seems worth reporting because information on the hazards of phosphine is limited and because other workers may hit on the ingenious idea of drying phosphine with calcium phosphide. Certainly if this method of drying is employed, fresh material should be used for every run.

U.S. Atomic Energy Commission Case History, quoted from ACCIDENT PREVENTION, Issue #53, January 1965, U.K. Atomic Energy Authority.

CASE HISTORY NO. 1067

Chemical Vapors Enter Work Area

Description: An employee was performing his regular work when he inhaled phosphorus oxychloride vapors. These vapors entered his work area when a tank car being thawed outside his building ran over. The tank car station was operated by employees of an adjacent building. The vapor exposure resulted in congestion of the respiratory system, similar to pneumonia.

Cause:

1. The phosphorus oxychloride was frozen in the tank car and needed to be thawed out before the car could be unloaded.
2. The car was not kept under surveillance during the thawing operation.
3. The tank car is loaded at 20-30°C.; therefore, the thermal expansion of the material during the thawing operation is critical.
4. The injured employee did not report for medical treatment after his exposure in spite of urging by his head operator. He did not realize phosphorus oxychloride had serious delayed effects.

Preventive Measures:

1. A representative of the vendor is coming to the plant location to provide technical service to help solve the problem.
2. New loading-unloading facilities will be installed to provide the necessary safety features.
3. A detailed unloading procedure will be written.
4. All employees in areas adjacent to phosphorus oxychloride facilities will be instructed in the hazards of the material and the importance of reporting for medical treatment immediately after an exposure or suspected exposure.

CASE HISTORY NO. 1068

Gas Explosion--Lighting Burner

Description: An operator attempted to light the pilot burner on a combustion chamber of a dryer. An explosion occurred when the lighted taper was inserted into the burner section.

Cause: Investigation revealed that the accident occurred as a result of the following:

1. Equipment failure - Safety shut-off valve remained open when unit was shut off. There is no open-closed indicator on valve.
2. Operator errors - (a) Failed to set temperature control on manual and set for low flow of gas to burner. (b) Opened block valve on main gas valve to burner before lighting pilot.

Preventive Measures:

1. Revise operating procedures and require all operators to follow these procedures. A written copy of procedures will be issued to each operator and a copy will be posted in control room.
2. The faulty safety shut-off valve will be replaced with a more positive closing type, equipped with a valve positioning indicator.

CASE HISTORY NO. 1069

Laboratory--Acid Handling

Description: A bottle washer was preparing to fill a three quart pan with a solution of concentrated sulfuric acid (55% Be) and potassium dichromate. This is a cleaning solution used for contaminated glassware.

The solution was still warm and was in a one-gallon glass jug.

The employee carried the jug to the sink counter and set it down. On grasping the sides of the bottle with both hands and lifting to pour it, the bottom fell away. The solution splashed and came in contact with the arms, legs and front part of the body.

The employee received third degree burns of both thumbs, second degree burns of all fingers on both hands and minor first degree burns of the legs.

Cause: The cause of this accident was the improper handling of acid and the lack of proper personal protective equipment.

The employee was not wearing gloves, apron or adequate face protection for the job she was performing. Handling of acid in glass jugs in this manner without a bottle carrier, etc. is contrary to safe practice.

The heat evolution of the solution could have provided sufficient thermal shock to the glass to permit it to crack when lifted free ot the counter, or setting it on a cold counter top, or a shock in setting it down could have contributed to the bottom separating on lifting.

Preventive Measures:

1. Written procedures for the handling of acids should be followed.

2. Personal protective equipment consisting of face protection, rubber apron, and gloves must be worn by any person engaged in similar operations.

CASE HISTORY NO. 1070

Employee "Loses" Eye Protection

Description: A pipefitter was lowering a small acid hose through a floor opening. As the hose was lowered, it struck an employee walking through the area and knocked his hard hat off. The employee's chemical goggle band was stretched around his hard hat; and the falling hat caused the goggles to slip away from his eyes, exposing them to 15% HCl running out of the hose. He received a severe chemical burn to his left eye and a minor burn to his right eye.

Cause:

1. Allowing hose to drop with acid flowing from it through a floor opening without first roping off or barricading the area, or seeing that warning signs were in place, or checking for personnel below.

2. Employee was wearing chemical goggle band around his hard hat.

3. The line this small hose was attached to did not have a valve or other means of stopping the flow of acid when repairs were necessary.

4. There was no written job procedure and the job line-up was inadequate.

Preventive Measures:

1. A general plant rule will be adopted requiring everyone using chemical goggles to wear the goggle band around his head.

2. On jobs where corrosive material could be a hazard, the area will be roped off.

3. A cut-off valve will be installed in this HCl line.

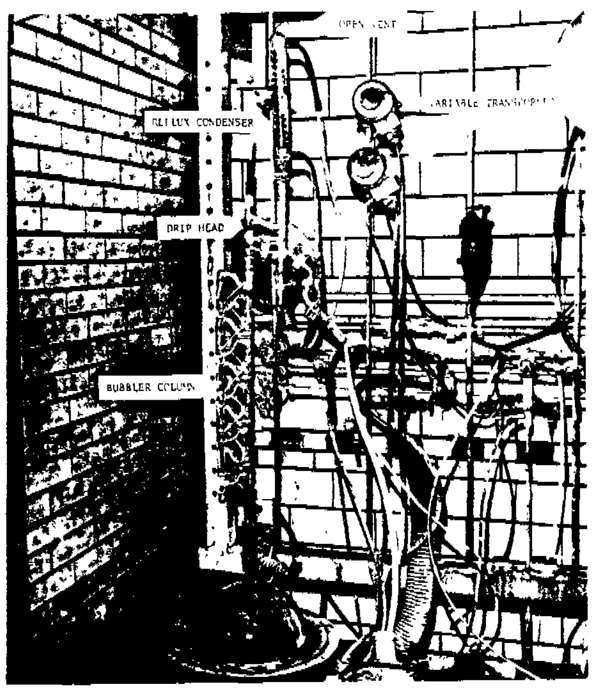
4. A job procedure will be written for this job.

CASE HISTORY NO. 1071

Variable Transformers in Hood Ignites Vapors

Description: An organic chemical being distilled in a laboratory hood was ignited presumably when the vapors contacted a variable transformer inside the hood.

The chemicals were being heated in a 22-liter flask. The vapors were passing through a bubbler column and a "drip-head." At the top of the drip-head there was a top-vented reflux condenser from which a small proportion of the condensate was being diverted to a 12-liter receiving flask (see picture).



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Cause: Material escaped from the top of the reflux condenser and contacted the variable transformer causing a flash fire to occur.

Preventive Measures: Relocate all variable transformers outside the hood. This is standard practice on all new hoods.

Condenser outlets should be vented directly to the exhaust plenum of the hood.

CASE HISTORY NO. 1072

Explosion in Centrifuge

Description: A foreman was about to look into the basket of the centrifuge extractor into which a slurry of material was being gravity fed when an explosion occurred. The flash burned the employee's left hand. Equipment damage was minor.

A slurry containing a solvent mix of 90% methylcyclohexane and 10% toluene was prepared in a reactor located on the mezzanine.

As the slurry was being gravity fed into the centrifuge, the chemical operator started to lean over the centrifuge to observe through the sight glass, when the explosion occurred.

The lid was lifted and flame released between the lid and the cover, burning the operator's hand.

The following details are of interest:

Approximately 60% of the batch had been fed in when the explosion occurred. The remainder of the batch continued to feed in after the explosion.

The centrifuge was a standard 48 inch rubber lined Tolhurst Center Slung Centrifuge being operated at 250 RPM at the time of the incident.

The fill line from the reactor is Teflon-lined stainless steel pipe running to a point three feet from the centrifuge where there is a gum rubber sleeve connector. The short connecting line from the sleeve to the centrifuge cover is stainless steel. The fill pipe within the basket is Saran, with a 45^{o} elbow. The spray nozzle inside the centrifuge is hard rubber. The 4 inch vent line to the unit is copper throughout.

The lid was clamped in two places only. The two clamps adjacent to the hinge were not in use.

The lid coating was cracked to a length of approximately 6 inches in from one clamp seat and the lid slightly warped in the same area.

The area of burning appeared to be within the basket. The hub, spray head fill nozzle, and filter bag turned black, showing evidence of charring.

The damper in the vent line was closed. Examination showed it did not have a tight fit and had a substantial draw. The line was blown free as a result of the explosion.

Cause: It was concluded that an explosion occurred in a flammable atmosphere within the centrifuge as a result of a static discharge and a resultant spark due to air in-leak.

Some areas of different electrical potentials which could have existed at the time of ignition and acted as the source are:

1. Between the Saran fill pipe and the grounded copper vent line;

2. Between the static charge established by the solvent driven through the filter bag, drum ports and against the insulated inner walls with any available ground or other object which was static charged.

The static-generating tendencies of hydrocarbon solvents were recognized as contributing to this incident.

The lined centrifuge was considered to have contributed materially to static accumulation.

Preventive Measures: 1. Future runs of this product and any other involving flammables will be done in a stainless steel centrifuge.

2. Steps will be taken to provide nitrogen blanketing of centrifuges.

CASE HISTORY NO. 1073

Contact Lenses

Description: A chemist, wearing contact lenses, failed to protect his eyes with safety glasses and had a speck of a corrosive material enter his eye. He removed his contact lens, washed out the affected eye and replaced the lens. Several hours later, while at home, his eye became very irritated. He again removed his contact lens and washed his eye but this time did not replace the lens. By the following day, his eye became very painful and he reported to the Plant Health Department. He has been hospitalized with a critical eye injury.

Preventive Measures: The doctor reported that the severity of the injury may have been greatly lessened:

1. If the injured had obtained medical assistance promptly instead of trying to treat himself.

2. If the contact lens had not been replaced following the initial washing. Contact lenses should never be replaced following any eye injury or irritation without medical advice.

The injury again emphasizes the importance of wearing eye protection in the chemical laboratory and especially when using contact lenses.

CASE HISTORY NO. 1074

Missing Gasket Leads to Vapor Exposures

Description: During a period of a month's time, two reactor operators received repeated exposures to methyl chloride vapors. These vapors entered their work area as a result of a leaking flange at a safety disc. The vapor exposures resulted in chemical poisoning to both men.

Cause:

1. Methyl chloride vapors entered the work area undetected from a leak in a flange at a safety disc.
2. The safety disc had been changed during this month's time and the employee had neglected to install a gasket.
3. The relay switch on the monitoring alarm system was burned out, making the system inoperative.
4. The symptoms of the methyl chloride exposures were not immediately apparent.

Preventive Measures:

1. The operators will note on a chart the corrective action taken whenever the monitoring instrument shows deviation from the safe level.
2. The alarm on the monitoring instrument has been supplemented with a flashing light.
3. All employees have been made aware of the importance of replacing gaskets after flanges have been separated.
4. All employees will be made knowledgeable of the hazards of methyl chloride.

CASE HISTORY NO. 1075

In-Plant Switching of Railroad Cars

Description: A crew was in the process of switching a tank car with a small Trackmobile. To get sufficient traction, shims are inserted between the car coupler and strikeplate above it, so that the Trackmobile's hydraulic coupler can exert sufficient upward pressure on the tank car coupler to keep the drive wheels from slipping. The strikeplate on this tank car had been broken upward; its full dimension giving a taper to the space between it and the coupler and reduced rigidity. Not one or two, but five steel shims were put into this tapered space. On pulling the tank car past an unusually sharp curve slightly uphill, three of the steel shims forcefully "squirted" out of the tapered space. Two of them went some 20 ft. and the third one, weighing 6-1/2 pounds, hit the brakeman who was standing ten feet from the coupler. He suffered a laceration across the point of the chin requiring 3 sutures for closure, a loosened front tooth, a cut gum and some jawbone injury. Had the blow been 2 inches lower or higher, the injury could have been much worse.

Cause: The taper of space and lessened rigidity of the strikeplate permitted shims to "squirt" out as pressure increased. This, in turn, was caused by the need for such action which sometime, someplace before had caused the strikeplate to break loose. And this was necessitated by the lack of traction by the small Trackmobile without vertical pressure on the car to be moved. Fourthly, the reduced radius of curvature of the railroad spur and the uphill elevation compounded the effort required to move cars at that point.

Preventive Measures: New shims of various sizes with chains attached for fastening to the coupler are being made. The preferred methods of inserting shims are being emphasized. Purchase of a heavier switching machine is under consideration.

CASE HISTORY NO. 1076

Use of Improper Equipment

Description: An employee was hand blending a small quantity of ignition mix, in a porcelain enameled bucket, with a brass scoop. The mix ignited causing burns to his face and both hands.

Preventive Measures: Stainless steel equipment will be used for this type of work.

CASE HISTORY NO. 1077

Dust Around Knit-Wrist Gloves Caused Chemical Burns

Description: An employee was cleaning powdered lime dust around the bottom of kilns. Dust around the top of knit-wrist gloves caused minor chemical burns on both wrists. The employee scrubbed skin from over the burned area. The burns on the right wrist became infected, requiring hospitalization.

Cause:

1. Unsafe dress or attire.
2. Improper protective clothing.
3. Aggravation of minor injury by employee.

Preventive Measures:
1. Canvas oversleeves will be used in the future on jobs of this nature.
2. Gauntlet chemical gloves will be used instead of knot-wrist type.
3. The employee will be retrained on this job.

CASE HISTORY NO. 1078

Asphyxiation--Breathing Air Cylinder Filled with Inert Gas

Description: Two operators were cleaning up a dichloroaniline spill on top of a tank car and the surrounding area. Full protective clothing and an air supplied hood were being worn by the operator actually engaged in the work. A second operator was stationed in the area as a standby. Immediately after changing his hood to a new air cylinder, the operator had trouble breathing. He removed the hood, caught his breath, and asked his standby to increase the flow from the cylinder. He then replaced his hood and resumed work. Shortly thereafter, the operator became dizzy and faint. He tried feebly to remove his hood. The standby rushed to the operator's aid, removed the hood, and assisted him down to the ground. The operator was pale and weak but quickly regained his breath. He was carried to First Aid where he was given oxygen and an injection of Fistaril for nausea and apprehension. After an examination by the plant doctor, he was released with no ill effects.

Cause: A sample from the cylinder was analyzed by the Laboratory. Analysis showed that the cylinder contained a mixture of 1 percent oxygen and 99 percent nitrogen. The cylinder was painted green with a blue top as were five companion cylinders of "enriched air" (a 30 percent oxygen mixture). The six cylinders had been delivered to the area from the cylinder storage shed to fulfill an order for six "enriched air" cylinders. Four of the five good cylinders were labeled correctly. The faulty cylinder was not identified in any way other than color code. An immediate check was made on all "breathing air" cylinders in the plant. All were found normal.

The plant was using both standard compressed air and "enriched air" for breathing. The supplier considers "enriched air" a special blend or mixture and not one of his eight basic gases. Compressed air is considered a basic gas. The plant's supplier, the only local source available, apparently filled the cylinder with the wrong gas (N_2) and delivered it to the plant as "enriched air."

Preventive Measures: Each cylinder of breathing air will be analyzed upon receipt. The safety and fire inspector will make the analysis and tag each cylinder as O.K. and show date of analysis. No cylinders will be issued for use unless they are so tagged.

In addition, breathing air cylinders will be painted orange and white in 6 inch wide bands and stencilled "Breathing Air" with 1 inch letters. Breathing air cylinders will be kept in locked building separate from all other compressed gases. Access thereto will be by permission of Stores Attendant only.

Only properly color-coded and identified cylinders will be accepted from the supplier. Identification in the case of mixtures must include a tag showing contents.

CASE HISTORY NO. 1079

Dumpster Operation

Description: Employee had just completed unloading a drum of adhesive in a storage tank with a special air-actuated dumpster used for drum raising, lowering, and tilting. Employee pushed the control level lowering the drum instead of pushing the lever to tilt the drum back to a vertical position. The drum caught on the storage tank and lifted the dumpster's front wheels off the floor. The bottom of the dumpster swung under the tank and it fell over backwards, pinning the employee under it as it fell.

Cause: The employee pushed the wrong control lever which caused it to tilt and fall over backwards. Also, the dumpster was not solidly anchored to the floor.

Preventive Measures:
1. Dumpster has been anchored fast to the floor.
2. Employees have been re-instructed in safe operation of dumpsters.

CASE HISTORY NO. 1080

Faulty and Improper Use of Equipment

Description: Four employees of the Electrical Department were installing a junction box. Two of the men were standing on the top of a panel board; another was operating a lift truck with the fourth man standing on a wooden pallet supported by the forks of the lift seven feet above the floor. When the job was completed, the man operating the lift truck moved it to a location where the man on the pallet could be lowered to the floor. The operator pushed the control to lower the forks, and instead of gradually lowering, they suddenly fell about five feet, coming to a sudden stop two feet above the floor. The man on the pallet was in a squatting position and the sudden stop caused him to fall to the floor. His injury consisted of a compression fracture in the lumbar region of the back.

Cause: Investigation revealed that the chain guide on the lift truck was out of the guide rail causing the chain to hang. When the down control was pushed to lower the forks, slack accumulated in the chain and suddenly released, dropping the pallet five feet.

Preventive Measures:
1. Fork lift trucks with pallet platform will not be used as an improvised scaffolding.
2. Defective equipment has been repaired and weekly inspections have been scheduled for all fork trucks, and load handling tools. This inspection will be carried out in conjunction with regular weekly inspections to cable and hoists.

CASE HISTORY NO. 1081

Compressor Operation

Description: A serious hand laceration and wrist fracture occurred when a millwright's hand was pinned by a moving piston in a hydrogen compressor. The compressor was being checked for malfunction. It was believed that one or more valves may have been reversed when previous work was performed on the unit. The injured removed a valve which exposed the chamber. An inert gas introduced into the feed line to check the valve action caused a hissing sound. The employee instinctively placed his hand through the open port to determine if he could feel the gas flowing. While doing so, the piston moved forward pinning his hand in the cylinder. Others present turned the flywheel to release the injured's hand.

Cause: A preliminary investigation revealed that the two intake valves were reversed and prevented the inert gas flow to the first stage. This caused the gas to enter a common line to the underside of the piston on the second stage, setting the compressor in motion. This line is to permit hydrogen, which blows past the second stage piston, to return to the first stage feed. The supervisors and the injured were unable to foresee the possibility of inert gas entering the housing and exerting sufficient pressure to move the piston. All switches were locked out and bleed valves on all stages were opened. The accident emphasizes the need for extreme care when working on pressure equipment.

CASE HISTORY NO. 1082

Operator Burned While Adding Reagent

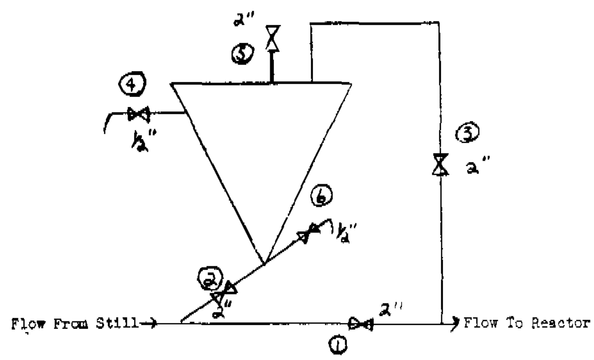
Description: An operator was seriously burned about the shoulder and arm when he prepared to drain oil from the reagent dispersing cone prior to the introduction of reagent to a reaction.

Approximately one-quarter to half pound of powder reagent is added to a system daily. The approved procedure – which apparently was followed – is to open valve one, (see sketch) close valves two and three tightly to divert flow from cone. Open valve four to drain oil into a pail. Open valve five slowly and carefully to vent chamber and to introduce reagent.

Oil came out of valve four so slowly that the operators assumed the cone was plugged with old undissolved reagent and proceeded to prod it with a stick through valve five. After two or three minutes' time, when very little oil had come through valve four, it was decided to close this valve and drain oil from valve six.

As the operator leaned over and opened valve six, a shower of hot oil, approximately two quarts, spurted from valve five. It was ascertained that the oil did not overflow slowly over the top and that no fresh reagent had been added. According to the witnesses, the operator was not burned by oil dripping from valve four. After the one violent spurt, no more oil came from valve five but another operator closed the valve as a precaution.

Preventive Measures: In order to make the present method safer, the operator will be required to wear a face mask and gloves. In addition, a new outlet will be installed on the bottom of the cone so all the liquid is drained from the cone before the reagent is added.



CASE HISTORY NO. 1083

Slipped and Struck Shin against Sharp Edge

Description: The employee had been shown locations for collecting laboratory samples in the acid plant. He attempted to step

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up on a filter foundation ring, a distance of 20 in. above floor level, when his foot slipped and his right shin struck the edge of the brick-covered ring.

Cause: Investigation of the accident revealed the cause to be:

1. Lack of awareness by the employee.

2. Wet floors.

3. Failure by supervision to recognize and correct potential hazard (20 in. elevation from floor to walkway around filter).

Preventive Measures: The floors were wet as a result of clean-up work following construction and start-up of new unit. This condition will improve as operational problems are eliminated. Access step to the filter foundation ring will be provided in two locations. The injury will be discussed at bi-weekly safety training classes for supervisors, and also at weekly safety meetings with hourly employees.

CASE HISTORY NO. 1084

Ruptured Hose--Sulfuric Acid Splash

Description: Sulfuric acid for the water treatment plant was needed as the steam and recovery unit was inoperative. The shift foreman, acting operating shift superintendent, and the injured attempted to fill two containers from the filter drain.

The rubber hose attached to this drain ruptured when the drain was opened and sprayed the injured man with sulfuric acid. His eyes were protected with safety glasses.

Cause: The action of the acid on the lining of the rubber hose caused the hose to collapse anf form a blockage. When pressure was applied, the hose ruptured at the point of blockage.

Preventive Measures: The hose will be removed and replaced with a permanent drain line to the sewer.

All workers will wear proper protective clothing when handling or working with acids. This will include full face shield, rubber gloves and rubber clothing.

CASE HISTORY NO. 1085

Pressure Surge Causes Hose to Whip

Description: An employee had climbed on top of a tank to take a measurement of material. Trisodium phosphate (165°F.) was being pumped into an adjacent tank through a hose which was wired to the tank. A pressure surge caused the hose to whip, breaking the wire. The material sprayed on the employee. He received first and second degree thermal burns to both thighs.

Cause: 1. The pump may have cavitated and then regained prime, causing the pressure surge.

2. The wire was inadequate to hold the hose.

3. There was no "tee" on the end of the hose to equalize the discharged pressure. (The "tee" prevents the whipping action by causing equal thrust in opposite directions.)

Preventive Measures: 1. The tanks have been fitted with couplings for direct hookup.

2. Whenever hoses are dropped in tank domes, they shall be properly secured and "teed" at the discharge end to withstand pressure surges.

CASE HISTORY NO. 1086

Gas Release--Sight Glass Failure

Description: At 12:40 p.m. the foreman noticed there was no pressure in #3 Hopper; almost simultaneously the gas alarm sounded and indicated a gas (flammable) concentration in #3 Bay. The unit was shut down immediately and an investigation revealed gas was passing from the Bay into an adjoining room. The outside door of the Bay was opened and when most of the gas had been cleared out it was discovered that the flat sight glass in the Hopper had shattered and blown out. No one was in the Bay at the time of the incident. The rating of the sight glass with respect to temperature and pressure is well above any operating conditions that could exist.

Cause: The sight glass had been changed four days before the incident. There was no spare available, and a used sight glass was cleaned and installed. Care was taken when cleaning the ground surfaces but it is doubtful if the glass was in "new condition." It is not always possible to ensure that the flat surfaces on the holding flanges are perfectly clean because of the urgency in changing the sight glass to prevent air oxidizing the contents of the hopper. It is, therefore, likely that the sight glass failed because of a concentrated stress, either due to unequal torque on the holding bolts or imperfect flat surfaces, or possibly a combination of these factors.

Preventive Measures: 1. An immediate investigation is to be made regarding the feasibility of pre-assembling the sight glasses in a redesigned holder in the Shops, where special attention can be given to prevent undue or unequal stresses. In addition, commercial designs are to be investigated.

2. Until Item 1 is resolved, the following procedures are to be followed:

   (a) Only new (or clean) gaskets are to be used when replacing sight glasses. Consideration should be given to the use of a softer gasket material.
   (b) Only new (or clean) sight glasses to be used. If sight glasses are reused the ground surfaces must be clean and not scratched.
   (c) The mating flat surfaces of the holding flanges must be clean, and are also to be checked for flatness.
   (d) Special care is to be taken to ensure that equal torque is applied to all bolts when tightening down. The wrench used is not to be longer than 8 inches.

3. The feasibility of checking sight glasses for high or concentrated stresses is to be investigated.

4. A face shield is to be worn when looking into the hopper through the sight glass. Face shields are to be mounted near each hopper for this purpose.

CASE HISTORY NO. 1087

Truck Operation

Description: An employee was operating a lead type power truck traveling north in a clear ten foot (10 ft.) wide aisle. To position the truck in order to back it into an elevator located west of the aisle, he started to make a sweeping U turn. Realizing too late that the path of the turning truck would not clear the projecting wall of a stairway enclosure immediately north of the elevator, the employee applied the brakes. The forward momentum of the truck was enough to catch the employee's foot between the truck and the wall.

Cause: The employee misjudged the truck clearance. (Correct procedure is to travel beyond the elevator, stop, reverse direction and then follow truck through a ninety degree turn as it backs into the elevator.) Although the employee was wearing safety shoes, metatarsal foot protectors would have provided more adequate protection.

Preventive Measures: This accident has been reviewed with all plant employees operating lead type power trucks, and correct way to operate these trucks was stressed.

CASE HISTORY NO. 1088

Implosion in Still During Cleaning Operation

Description: A five thousand gallon stainless steel solvent recovery still imploded during cleaning operations. The vessel was designed for 14.5 lbs. pressure but not for vacuum. It was vented through separate two inch vents with flame arrestors on the condenser, the reflux tank, and the receiver, but all the vents were on the same line from the vessel.

Previously, boiling water had been used to clean out the vessel whenever repairs were necessary. However, on the date of the incident steam at approximately 100 lbs. pressure was directed into the vessel and through the column and condenser for about 15 minutes. The steam hose was disconnected and the condensate drained from the vessel and column. Cold water was applied to cool the vessel and after the water had been turned on for a few minutes, the tank collapsed.

Cause: The contraction of the vapors due to the sudden cooling caused a partial vacuum since the total venting capacity was inadequate.

Preventive Measures: Ample size vents as well as a vacuum breaker have been provided on the replacement still. Engineering Standard MP-7 indicates minimum vent sizes required to prevent collapse due to sudden cooling.

CASE HISTORY NO. 1089

Fluorine Leak

Description: On Thursday, a new fluorine feed cylinder was installed in the aqueous fluorination system. The two pressure regulating valves in the line from the cylinder were closed and the main cylinder valve was then opened. A fluorine leak was detected and an attempt to close the main cylinder valve was made. However, it could not be closed tightly enough to stop the leak. The cylinder was left to leak down over the weekend, but the fluorine odor still persisted on Tuesday morning. The fluorine was disposed of Tuesday night by reopening the main valve and the pressure regulators (using a Scott Air Pak), metering the fluorine to the reactor hood in the usual manner, and exhausting to the atmosphere. Since the fluorine feed area was purposely located in an isolated area and the main valve remotely operated, there was no personnel exposure or curtailment of other operations in the building as a result of the incident.

Preventive Measures: As a precautionary measure, a leak test of the piping and fittings will be made in the future prior to opening the main cylinder valve.

Armed Services Explosives Safety Board Case History.

CASE HISTORY NO. 1090

Sampling

Description: As an employee was attempting to take a sample from a hopper, above a rotary valve in a silo airveying system, he dropped the sample cup. In attempting to retrieve the cup his fingers were caught and cut by the rotary valve.

Cause: The employee was not aware of the hazard and failed to comply with previous instructions he had received to shut down the equipment prior to taking a sample.

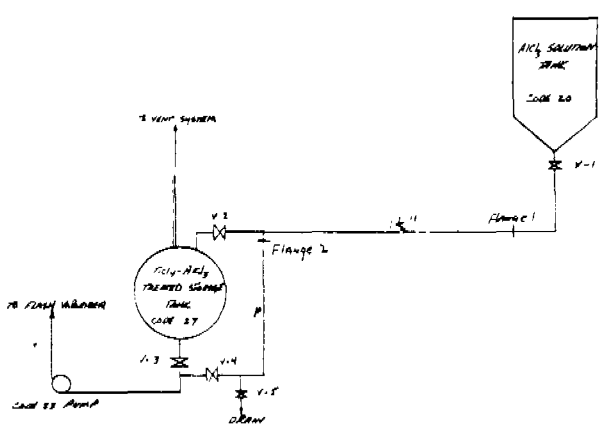
Preventive Measures: A protective barrier grid has been welded across the throat of the hopper above the rotary valve.

The job safety analysis of this operation has been reviewed to make sure all of the safeguards have been covered and has been reviewed with all personnel concerned.

CASE HISTORY NO. 1091

Fume Release from Pipeline

Description: Maintenance operating personnel were checking a corrosive liquid product pipeline to determine the reason for a block in the line. (Refer to sketch) V-1, v-2, v-3, v-4 were closed and v-5 was open. From a platform on top of code 27 above flange No. 2,



the employee proceeded to open flange No. 2. Three bolts had been removed from flange No. 2 and when the last and fourth bolt was loosened, there was a "puff" of irritating fumes that came from the opening and struck the employee in the face. The employee had to make his exit through a fumigated area due to the wind direction at the time.

Cause:

1. Employee did not wear the personal protective equipment required.
2. The vent system was blocked up and under a slight amount of pressure.
3. Failure of employee to attempt to bleed pressure from the pipeline prior to starting the work.

Preventive Measures: Henceforth, whenever a corrosive product line is to be opened, personal protective respiratory equipment will be worn.

A job safety analysis will be made of the maintenance operation to make sure all of the safeguards are considered which will be reviewed with all concerned personnel.

CASE HISTORY NO. 1092

Working on Pressurized Column

Description: A dial thermometer which indicates temperature in one column of a two-column instrument was out of order. One column of the instrument air dryer is always in operation, drying compressed air at 100 psig. One column is always being regenerated with hot air at a pressure of about 3 psig.

An electrician, assisted by the operator, removed the dial thermometer of the column with 100 psig air pressure, and silica gel was blown against the operator's forearm and body. His injuries consisted of abrasion and tissue damage to the left forearm and slight damage to the abdomen and the left thigh.

Preventive Measures: This accident will be discussed in detail at Departmental Safety Meetings and employees will be encouraged to think clearly before proceeding to perform work.

CASE HISTORY NO. 1093

Ruptured Air Mixing Chambers

Description: Air mixing chambers on the recycle lines to primary oxidation furnaces ruptured. Air and recycle gases, mostly propane and butane, escaped. Gases were ignited and flashed back to the ruptured area.

The fire burned until the available hydrocarbons were consumed. The process had been shut down from a control room. Remaining pressure was vented off to the flare stack and quench steam was added to the recycle lines.

Apart from the recycle lines, damage consisted mainly of electrical and pneumatic instrumentation plus the lighting fixtures and damage to the valve house containing oxygen addition controls.

The air mixers are located on a pipe rack approximately sixty feet west of the PO building compressor wing and between the furnaces and oxygen plant warm building. This location, plus the fact that the lines ruptured at the top directing the flames mainly upward, together with prompt action of operating personnel, combined to minimize the damage.

Cause: Gases were ignited from any one of a number of possible sources, e.g., static, 600 psig, steam lines or a furnace.

Heat developed in the jacket portion of the mixer sufficient to soften and weaken the metal, allowing it to rupture at the normal operating pressure of 140 psig. Heat from the fire quickly caused the adjacent "A" mixer line to fail in similar fashion.

The design of the mixer, and a rare combination of conditions never previously encountered, led to developing heat in the jacket of the mixer. The mixer is merely a perforated section of the recycle line itself. Air comes into a jacket around this section and enters the hydrocarbon stream through the perforations. It is quite possible for hydrocarbons to weep through into the jacket and mix with the incoming air.

Normally, this would not matter. The main recycle stream being well below the ignition temperature for the mixture, the procedure is considered to be safe. Given a source of ignition, which can only be guessed at, for example, a metallic particle or deposit of carbon, or a trace of oil in the airline, it would be possible to have a combustion in the air rich mixture in the jacket. There is clear evidence this did happen, and excessive temperatures built up in the jacket only.

Preventive Measures: The method of adding air to the recycle stream has been changed. Jacket mixer has been replaced by an internal pipe sparger which provides much more efficient air mixing. This also eliminates the possibility of any significant temperature buildup even in event of any recurrence of an ignition within the air sparger itself.

CASE HISTORY NO. 1094

Flash Fire While Adding Catalyst

Description: A flash fire occurred while adding catalyst on charcoal to a still and burned a chemical operator's face and ear. The catalyst ignited as he was charging the material from a plastic bag to a reactor containing a caustic solution under a blanket of nitrogen.

Cause: In the absence of flammables, it is believed that a static spark ignited the charcoal dust.

Preventive Measures: The charging procedure has been changed to slurry the catalyst in water in a metal container before adding to the still. The injured was fortunate in not having suffered a serious eye injury, as he was not wearing the prescribed face shield.

CASE HISTORY NO. 1095

Laboratory Chemist Sprayed with Molten Salt

Description: Molten salt mixture at 580°C erupted and burned a chemist's hands, face, neck and chest. The chemist lowered a small stainless steel U tube reactor into a one gallon capacity salt bath. While tightening the clamp, the batch erupted covering his hands. Some of the molten salt also sprayed on his face and body, but he was wearing eye protection and this saved his eyes from serious injury.

Cause: It is believed that the high temperature mercury thermometer broke and the vaporization of the mercury under the surface of the hot salt caused the bath to erupt.

Preventive Measures: The use of all mercury thermometers reading over 360°C should be discontinued and dial thermometers or thermocouples substituted.

CASE HISTORY NO. 1096

Near-Miss Fire Loading Truck With Methyl Alcohol

Description: A common carrier's tank truck had just completed loading methyl alcohol when smoke was noticed coming from beneath the truck tractor. Battery cables had shorted and set fire to the grease/oil-laden cables and to the under framework of the tractor. Fortunately, the tank hatch had just been secured; had loading still been in progress, a very serious fire and/or explosion could certainly have occurred with disastrous results.

Due to the inaccessibility of the fire area, final extinguishment was made by the operators lying on their backs under the truck. The driver had no fire equipment on his truck, nor did he participate in putting the fire out. It was necessary to use 150 lb. and 20 lb. dry chemical units, as well as one 15 lb. CO_2 unit.

Preventive Measures: Common carriers serving our chemical terminals have been notified of this incident and have been reminded of their responsibility for closer inspection and maintenance of their vehicles, of the legal requirement for fire equipment on tank trucks and for driver training in the use of same.

CASE HISTORY NO. 1097

Explosion--Hydrogen Gas

Description: Following the termination of a process utilizing hydrogen, an open air explosion occurred in the vicinity of the hydrogen gas vent stack. The explosion caused severe damage to several buildings in the proximity of the facility and slight damage to walkways, small beams, and cabinets in the vicinity.

Cause: During the normal process, cold gaseous hydrogen is vented through a vent stack into the atmosphere. Normally hydrogen is bled through a piping system and into the atmosphere for approximately 45 minutes at which time the process is completed.

During this particular occasion, an unusually calm weather condition (no wind) prevailed. It is theorized that this calm weather condition failed to disperse the hydrogen gas as rapidly as usual. This gas accumulated in the atmosphere overhead and was then ignited by an unknown ignition source, creating the explosion.

Preventive Measures:

1. Venting or bleeding of hydrogen gas will be accomplished only when a sufficient amount of turbulence exists to disperse the gases.
2. Studies to determine the relative advantages of burning vent-gases versus releasing gas only during conditions of predetermined wind velocities will be continued.

Armed Services Explosives Safety Board Case History.

INDEX

The contents of this Index have been carefully compiled and organized to give maximum assistance to readers searching for accident case histories involving specific chemicals, specific pieces of equipment, or specific occupations.

To find a case history of a particular nature, look first under the group category most closely associated, e.g. Chemical, Operation or Occupation, Equipment, Explosions and Pressure Releases, Fires, Static Electricity, Waste Disposal, Corrosion, or Protective Equipment.

The same accident case history may appear under several categories. For example, accident case history No. 660 appears under the "Chemical" category as "acetaldehyde", under the "Operation or Occupation" category as "venting", and under the "Explosions and Pressure Releases" category as "acetaldehyde."

Many accident case histories, particularly those involving occupations or equipment failure, are not easily identifiable and may appear under various listings. For example, a particular case history may be listed under "pipe" or "line" or perhaps "valve" or "gasket." Similarly, a case history involving "hose failure" may appear under "loading", "unloading" or "transfer" etc.

For Accident Case Histories Nos. 1 to 596, see Volume One - 1962

CHEMICALS

OPERATION OR OCCUPATION

CMA 048513

EQUIPMENT

EXPLOSIONS & PRESSURE RELEASES

For Case Histories 1 — 596, see Volume I

FIRES

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