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MONSANTO COMPANY - PLASTICS DIVISION - SPRINGFIELD, MASS.

POLYVINYL CHLORIDE
PRODUCTION TECHNICAL SERVICE

PROCESS SAFETY AUDIT
POLYVINYL CHLORIDE POLYMERIZATION
July, 1964

Reported By: A. P. TORRENZANO

Date Issued: August 20, 1964

ABSTRACT

This report summarizes the current process safety hazards and a schedule for corrective action. In addition, reference information was compiled to aid in safe raw material handling procedures and design.

RSV0023888

TO: R. A. COFFEY (2)

Distribution:

A. W. Coaker	K. W. Howes
O. P. Cohen	N. G. Lieberman
R. A. Derrah	E. K. Mahlo
A. G. Erdman	D. E. Philpott
A. O. Ericksberg (15)	L. E. Rademacher
W. F. Gabel (2)	F. L. Turner
H. E. Greenwell	W. P. Willis
C. G. Hallen	Safety Dept. (2)

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I. INTRODUCTION

A process safety audit was initiated at the request of Mr. H. E. Greenwell following a series of process oriented hazards in the Plastics Division during June 1964.

The objective of the audit was to insure proper translation of process technology into safe, reproducible Manufacturing operations.

II. SUMMARY AND CONCLUSIONS

The audit was conducted in the following manner in order to detect hazardous operations.

- A. The 1957 process safety audit report was reviewed.
- B. The proper procedures for handling the hazardous PVC raw materials were defined and compared to actual plant practices.
- C. The Tentative Processes were compared to standard operating procedures.
- D. Discussions were held with supervisors to define polymerization hazards.
- E. Simpler, faster and more effective emergency procedures were sought.

In practically all cases the known technology has been translated into safe equipment design and up-to-date operating procedures. The areas requiring further decisions and/or improvements have been listed in Section III of this report.

In summary, the audit showed that numerous safety improvements have been effected during the past seven years; one of the most important has been the introduction of styrene short-stop agent. Naturally VCM continues to be the major potential hazard in the area; new potential hazards introduced recently are: THF, A-6 catalyst, DEM and NH_4OH . Raw material handling has been monitored closely but some additional safeguards are necessary, as described in Section III.

The two most probable significant hazards in the polymerization area have been active PTS projects: the accidental dumping of the wrong kettle; the spontaneous combustion of asbestos saturated with glycerine.

Nominal equipment modifications are recommended to the short-stop addition system, emergency instrument gas supply and kettle jacket instrument air supply to provide improved emergency procedures.

III. RECOMMENDATIONS

Current hazards and recommendations have been summarized in Table 1 together with decision or completion dates for each items as assigned by Messrs. W. F. Gabel, R. A. Coffey, K. W. Howes and F. T. Molyneux.

TABLE 1
SUMMARY OF PROCESS SAFETY HAZARDS
July 1964

<u>HAZARD</u>	<u>COMMENTS</u>	<u>ACTION</u>
<u>A. Raw Materials</u>		
1. Chronic VCM leaks at gasholder during past year.	Need permanent solution to stress failures in dome of gasholder.	Plant Eng. Proposal: 9/30/64
2. Essentially unrestricted traffic on road south of VCM unloading dock.	Review traffic requirements and impose necessary restrictions.	Production Implement: 10/1/64
3. No dike protection at: (a) 88 Bldg. VCM tanks (b) Tank farm pump hose (c) 84 Bldg. VCM tank	Problem is compounded further by the inability to isolate area sewer system from remainder of the plant in case of major VCM spill; no disaster communication procedure with north and west plants if "VCM sewer" problems should occur.	Production Decision: 10/1/64
4. Potential explosion hazard in copolymer dryer and storage hoppers via diffusion of VAc monomer from product.	Extent of problem not fully known; need measurements and recommendations to minimize the danger (air spargers, explosion vents, re-inforcement, procedure changes, etc.)	P.T.S. Complete Study: 11/15/64
5. Odor of DEM in A-6 dissolving room.	Improved housekeeping program necessary.	Production - 9/15/64
6. Erroneous use of DAM for DEM in A-6 dissolving.	a. Highlight DEM drums b. Study the extent of danger involved in dissolving A-6 in DAM.	a. Prod. - 9/15/64 b. PTS - 10/15/64 (Res.)
7. Spillage of L2O2 at the "delayed catalyst bomb" area in 92 Bldg.	Further improvement in handling equipment required.	Plant Eng. Proposal: 2/1/65

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TABLE 1 (Cont'd)

<u>HAZARD</u>	<u>COMMENTS</u>	<u>ACTION</u>
8. Possible spillage of L2O ₂ or A-6 solution during maintenance of catalyst charging equipment.	In addition to precautions defined in SDP, special supervisory attention should be required before the start of any maintenance work on catalyst charging equipment; use of "permit" possible approach.	Production - 10/1/64
9. At times, noticeable concentration of NH ₃ fumes in operating area during emulsifier makeup.	Improvement in draft system and/or lower temperature reaction control necessary.	Production Proposal: 11/15/64
10. Inadequate facilities for cleanup after NaOH weighing in 84 Bldg. raw material room.	Should attempt to replace this hazardous material in the Opalon 440 process with sodium bicarbonate. If not possible, improve weighing station for NaOH.	Production - 9/15/64
11. Lack of protective equipment when handling lime.	Operators occasionally fail to use eye protection during lime slurring operation in 92 Bldg.; re-emphasis of caustic dangers required.	Production - 9/15/64
12. Potential danger of set-up batch by using wrong raw material (such as antifoams) for C-1 charges.	Overall problem of housekeeping, warehouse storage, inventory control, identification and transporting of raw materials to kettle floor should be reviewed and improvements made. Large volume of antifoams, G-62, glycerine and C-1 being handled on 55 gal. drum racks; small raw material elevator in 88 Bldg.; lack of space on kettle floor results in no definite location for each raw material.	Production Define Program: 11/1/64

TABLE I (Cont'd)

<u>HAZARD</u>	<u>COMMENTS</u>	<u>ACTION</u>
13. Potential danger of set-up batch by using contaminated drum for G-62 packaging	Same as Item 12 above	Same as Item 12
<u>B. Polymerization Area</u>		
1. Accidental dumping of reacting batch.	Active PTS project already underway to provide automatic mechanical safeguard.	PTS Proposed Solution: 11/15/64
2. Spontaneous combustion when asbestos is saturated with glycerine.	A safe replacement for glycerine is now being tested using G-62 as the new dura-seal lubricant.	PTS Complete Evaluation: 12/1/64
3. Corrosion of deglassed, steel areas in Pfaudler reactors.	Define and start implementation of a program to upgrade all PVC reactors via nickel plating.	Prod. & Plant Eng. Program: 11/15/64
4. Mischarge or omission of B-1 or B-2 causing batch setup.	Study and revise the suspending agent charge system to prevent accidental sewerage of the charge; greater probability of undetected error now with the closed manhole raw material charging technique.	PTS Complete Study: 11/15/64
5. Open dump valve at start of raw material charge sequence leading to VCM leakage.	Consider a "permission switch" to detect or prevent charging of process water with an open dump valve; greater probability of undetected error now with the closed manhole raw material charging technique.	PTS Proposed Solution: 11/15/64

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TABLE 1 (Cont'd)

<u>HAZARD</u>	<u>COMMENTS</u>	<u>ACTION</u>
C. <u>Emergency Procedures</u>		
1. Improvement: Styrene Injection System	A styrene short-stop charge system should be installed on the step bearing flush line to provide faster, simpler and better protection during any multi-kettle emergency; simultaneous injection into all kettles can be effected in less than one min.	Plant Engineering Proposal: 12/1/64
2. Improvement: Air Failure Emergency	Faster switch-over to an emergency gas supply can be obtained by connecting the newly available plant nitrogen supply line in 88 and 92 Bldg. into the instrument air supply manifold; valving and pressure reducer will be necessary.	Plant Engineering Proposal: 12/1/64
3. Improvement: Full Cold Water	By installing a block valve on the instrument air supply valve all jacket water dump valves can be made to "fail-safe" quickly.	Plant Engineering Proposal: 12/1/64
	NOTE -- It would be desirable to install the above features, together with other safety devices at a centralized panel to permit the execution of all emergency operations in a matter of seconds.	

IV. SOURCES OF INFORMATION

1. Tentative Process, Opalon 9651 and 9661, April 1964
2. Tentative Process, Opalon 740, December 1962
3. Tentative Process, Opalon X-75, November 1960.
4. Tentative Process, Opalon 440, November, 1960.
5. Tentative Process, Opalon X-24, March 1962.
6. Chemical Safety Data Sheets, Mfg. Chemists' Association
 - SD-9 Caustic Soda
 - SD-13 Aqua Ammonia
 - SD-14 Trichloroethylene
 - SD-31 Acrylonitrile
 - SD-34 Styrene Monomer
 - SD-56 Vinyl Chloride
 - SD-75 Vinyl Acetate
7. Status Summary, Fast Catalyst PVC Homopolymer Process, Storage and Handling Phases of Isopropyl Percarbonate (IPP), O. W. Gruebmeier, L. Vartanian, August 12, 1963.
8. Technical Bulletin 350 - Isopropyl Percarbonate, Pittsburgh Plate Glass Co., Chemical Division, 2/23/62.
9. Dangerous Properties of Industrial Materials, N.I. Sax, Reinhold Publishing Co., 1963.
10. duPont Technical Bulletins, Electrochemicals Department
 - a. Physiological Properties of Tetrahydrofuran - Furan Products, FC2-1060
 - b. Tetrahydrofuran, Recommended Handling Procedures - Furan Products, FC3-161
 - c. Bulk Storage and Handling of Tetrahydrofuran - Furan Products FC5-260
11. Discussions with the following personnel:

V. E. Boyen	O. W. Gruebmeier
R. H. Cloutman	G. G. Hallen
R. A. Derrah	D. E. Philpott
W. F. Gabel	V. P. Phillips
H. E. Greenwell	L. E. Rademacher

V. REVIEW OF 1957 PROCESS AUDIT

The extensive process safety audit performed in 1957 was very helpful to our present audit. Since most of the plant equipment, basic operating procedures and raw materials have not changed in the past seven years, the potential process hazards listed in 1957 audit were still timely comments.

Much has been done to reduce the probability of experiencing a process problem and to minimize the severity of the dangers. Probably the most important safety improvement since 1957 was the introduction of a short-stop agent. It is now possible to terminate a polymerization within a matter of minutes and thus reduce greatly the dangers of out-of-control batches. For example, a power failure in 1957 could cause 10 to 15 batches to be out-of-control for hours; it is now possible to render all batches to a "dangerless state" within a short period of time.

The 1957 process audit does focus present attention to the VCM storage area where some questionable practices still exist. These and other potential hazards listed in the 1957 were summarized in Table 2, together with comments on current status.

TA 2
1957 PROCESS AUDIT HAZARD AND PRESENT STATUS

1957 Potential Hazards & Notes		No Change	Improved	Corrected	Comment on Current Status
A. Raw Material Category					
1.	Large VCM spillage at tank farm and polymerization constitutes the greatest hazard to the FVC area.	X			Four additional raw materials of significant potential hazard have been introduced into FVC area: A-6, THF, DEM & NH ₄ OH; however, VCM still presents the greatest disaster hazard to the area.
2.	Spotting of numerous VCM tank cars throughout the plant; tanks are known to leak VCM.		X		With the newer, larger cars in present service the degree of leakage has been reduced; however, the control of number of tanks in the plant should be reviewed and a practical solution defined.
3.	VCM tanks & lines not properly grounded.			X	No comment.
4.	Need sprinkler system over VCM tank cars spotted at dock.	X			Make decision and implement, if necessary.
5.	Yearly inspection of VCM tanks behind schedule.			X	No comment.
6.	Need better communication & traffic control in the event of an emergency condition.			X	Disaster control program being updated again by South Plot Safety Council following recent emergency in area.
7.	No means for safe emergency vent of a tank during stack line repairs.	X			There are additional ramifications to fact that there is only one safe emergency vent system; should the stack line be down for repairs or out of service due to pluggage or rupture (via an explosion in one building), the only other vent point of reactors is into the kettle room. This problem should be studied further with the consideration of a rooftop vent for secondary relief in the event of stack line failure.
8.	Unrestricted motor vehicle traffic south of VCM unloading dock.	X			This is not a wise practice when tank cars are being unloaded. Area safety council should define and implement traffic control.
9.	VCM thermal expansion cause excessive			X	Relief device installed.

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	No Char	Im e	Corre e	
10. VCM overflow of gashold possible via operator error.		X		Although operator error still possible, gasholder level warning system in operation in each area.
11. L ₂ O ₂ shed overloaded and not properly secured.			X	New building located in remote area.
12. Bz ₂ O ₂ in L ₂ O ₂ drum introduces a shock sensitive material into the area.	X			Remote possibility of supplier error.
13. VAc inhibitor level not tested.			X	Specification and testing of VAc under good control.
14. Need better communication between Control Lab, Research & Production on control of new raw materials.			X	Project Board responsibility in the area very well defined.
B. <u>Process and Equipment Category</u>				
1. General problems with formulation errors		X		Now have short-stop agent to reduce the batch control problem; better raw material quality control, esp. VCM, and checks on charging equipment; less sensitive suspension system for homopolymer; quantitative test of PDR-1 charge in copolymer; better SOP and better trained personnel.
2. Power and/or water failure severe hazard.		X		Use short-stop agent.
3. Emergency procedure for water and instrument air failure not posted.			X	No comment.
4. Adequacy of stack questionable for major emergency.			X	Equipment study shows system to be adequate.
5. Inspection of stack lines and knock-out tanks not scheduled adequately.			X	No comment.
6. Accidental dumping of wrong kettle severe hazard.	X			Active project to eliminate this possibility via automatic lock of dump valve when kettle pressurized.
7. Agitator speed limitation unknown.			X	Safe practice in plant.

	No Cha	I	Corr	
8. Dumping of excessive paste latex lumps to sewer.			X	No comment.
9. No emergency lighting in 92 Bldg.			X	No comment.
10. Copolymer fires in rotary dryers		X		Reduced the probability of a fire by mechanical control of air flow to prevent backdraft or resin onto heaters; possibility of fire still exists.
11. High volatiles in copolymer and Opalon 306 a hazard in silos and hoppers.		X		Product volatiles level much lower (2.5% down to 1%) nevertheless flammable concentrations may still be possible. This fact, together with the possibility of a fire in copolymer line, constitutes an explosion hazard. A study is required to define the severity of potential hazards and implement corrective measures (air sparging may be entirely adequate
12. Higher temperatures and pressures in processes reducing safety margin.		X		In the "Safety Ledger" faster, more complex processes must definitely enter in the debit side; better technology, more effective safety devices, better training of operators and better procedures are entered in the credit side. Since no quantitative figures are available, the opinion of the author is that a positive balance exists compared to 1957. Process safety "follow-up" is an area that merits further attention +
C. <u>Personnel</u>				
1. Insufficient experienced supervisors to handle fully the operation and safety training.			X	Supervisory and PTS group sufficient and well qualified to perform the job.

VI. DISCUSSION ON THE PROCESSING OF HAZARDOUS RAW MATERIALS

Of the 32 raw materials used in the PVC polymerization area, nine are considered significant potential hazards. The prime hazards associated with each are listed below. Four of the materials (THF, A-6, DEM and NH_4OH) are relatively new in the area.

<u>Raw Material</u>	<u>Hazards</u>		
	<u>Stability</u>	<u>Fire & Explosion</u>	<u>Toxicity or Burns</u>
VCM		X	
VAc		X	
THF	X	X	
A-6	X	X	
L_2O_2	X	X	
DEM			X
NH_4OH			X
NaOH			X
$\text{Ca}(\text{OH})_2$			X

A. Vinyl Chloride Monomer

1. Introduction

Without doubt, the greatest potential hazard in the area is fire and explosion caused by the ignition of VCM spillage. By nature, the PVC area contains over one million pounds of VCM and an explosion could damage the storage equipment and supply more spillage. Any large VCM fire is almost impossible to extinguish due to the high volatility and low ignition temperature of VCM; fire control is directed at eliminating the source of the VCM spillage and preventing the fire from spreading.

Any large VCM spill presents a plant-wide hazard via the sewer system.

Most disastrous accidents experienced throughout the world with VCM originated in the reactor room. This year an explosion at a Thompson Chemical Co. plant resulted when a glass inspection port failed and released thousands of pounds of VCM into the room; equipment failure followed and the VCM vapor was ignited. The ensuing fire and explosion killed seven employees.

A few years ago a plant in Japan was destroyed when a reactor was accidentally opened releasing VCM into the area. The same sort of accident occurred in a PVC plant in Italy but fortunately the VCM vapors were not ignited. An explosion occurred in Springfield many years ago when a tank was overfilled allowing VCM vapors to concentrate in the area; fortunately, no fatalities resulted.

VCM leakage in the polymerization can be caused by (1) uncontrolled reactions, (2) equipment failure, and (3) operational error. All three cases were studied during this audit and recommendations made in the appropriate sections of this report.

2. Physical and Chemical Properties

Molecular Weight 62.5
 Critical Pressure 52.7 atm.
 Critical Temperature 158.4°C (317°F)
 Boiling Point -13.8°C (+7°F)
 Color Colorless or water-white
 Odor Sweet smelling gas
 Physical State Gas at ordinary temperature and pressure -- Liquid under pressure in cylinders or pressure vessels at room temperature.
 Freezing Point -153.7°C (-245°F)
 Specific Gravity9121 at 20°/20°
 Vapor Density 2.15 (air = 1.0)
 Vapor Pressure 2580mm of mercury at 20°C
 Flash Point -78°C (-108.4°F), Open-Cup
 Explosive Limits Lower 4%; Upper 22%, by volume in air.

3. Hazardous Properties (Summary)

a. Health Hazard

Aside from the risk of fire and explosion, vinyl chloride presents no other serious problem in general handling. The threshold limit value is 500 ppm.

In concentrations well above 500 ppm vinyl chloride acts as a mild general anesthetic.

In contact with the skin vinyl chloride is irritating. Prolonged contact will result in refrigeration and freezing.

b. Fire Hazard

Vinyl chloride vapors form flammable mixtures with air at all temperatures above -78°C.

Fires involving large quantities of liquid are almost impossible to extinguish; it is usually necessary to stop the source of VCM leakage. RSV0023903

4. Key Points for Safe Handling

- a. Keep away from heat, sparks and open flame.
- b. Electrical equipment should conform to the National Electrical Code, Class I, Division II for storage and Class I, Division I for use.
- c. Provide adequate ventilation.
- d. Ground equipment and containers before discharging to reduce danger of ignition from static sparks; resistance to ground should never exceed 25 ohms.
- e. In discharging, do not heat containers above 50°C. No heat should be applied to tank cars.
- f. All equipment should be steel and have a designed working pressure of at least 100-150 psi; no copper or silver allowed; no glass equipment such as rotameter and sight glasses allowed.
- g. Storage tanks should be protected with a water spray system. Adequate diking should be provided under tank area in case of vessel rupture. For spill control, all openings in sewer system should be trapped for segregation and extinguishment.
- h. Do not enter spillage area without proper respiratory protection.
- i. Chemical safety goggles should be worn when discharging containers or tank cars or sample taking.
- j. Frequent inspections of equipment and vessels containing vinyl chloride should be made to detect or prevent leaks. Note that vinyl chloride is generally non-corrosive at normal atmospheric temperatures when dry (moisture-free). However, mild to appreciable corrosion has been noted; this may be due to the presence of impurities. In contact with water at elevated temperatures, vinyl chloride accelerates corrosion of iron or steel.

5. Specific Hazards with VCM Storage & Handling at Springfield

- (a) Recovered VCM gasholder leaks have been a chronic problem during the last year.

Solution: Permanent upgrading of facilities required.

- (b) Vehicle traffic on the road immediately south of tank farm essentially unrestricted.

Solution: Review traffic requirements in this area -- eliminate or reduce

- (c) No dike protection in the following locations:
 (1) "washed" VCM tanks west of 88 Bldg., (2) tank farm pump house, (3) VCM tank east of 84 Bldg.
 Problem is further compounded by inability to isolate sewer system in area from remainder of plant. In addition, there is no formal procedure for communications with other sections of the plant in the event of large VCM spillage.

Solution: Request study of the situation by area safety council.

- (d) Recommendation: Once per year, the area monthly safety program should be directed at:

- (1) Meeting - "Safety in Handling VCM", covering the proper techniques for VCM transfer and sampling, fire and health hazards, protective equipment and emergency procedures for VCM spillage and/or VCM fire. Personnel should include Production, T & M and Maintenance.
- (2) Report - condition of present VCM storage and handling equipment; condition of safety equipment.

6. Specific Hazards with VCM in Polymerization Area

See Section VII, "Polymerization Hazards".

B. Vinyl Acetate Monomer

1. Introduction

Vinyl acetate has been employed for many years in the production of Opalon 500 series copolymers. During the last two years VAc monomer has been supplied solely by Texas City to the Springfield operation. Improved storage and handling equipment have been installed during the years and better raw material quality control has been defined.

No significant accidents have been experienced with VAc during the storage and handling of this material. In the polymerization area, the dangers of this material are "covered" by the more difficult co-monomer, vinyl chloride. It should be noted that the copolymer polymerization suspension system is sensitive to raw material impurities and operating conditions. Out-of-control polymerizations usually result in rapid fusion of the slurry particles and the reaction mass behaves more like a polymer melt than a suspension. As a result, pluggage of the emergency vent system may occur and the ensuing high pressure buildup can cause serious equipment damage with VCM and VAc leakage.

The presence of occluded monomers in the copolymer particles presents a potential hazard in the drying and storage of the product. Explosive concentrations are possible by the diffusion of these monomers into the air space above the product.

Experience has shown that heat degraded copolymer can be ignited by contact with air temperatures in the 120-160°C range.

2. Physical and Chemical Properties

Molecular Weight	86.1
Physical State	Liquid at ordinary temp. and pressure; clear and colorless
Critical Temperature	228.9°C (444°F)
Critical Pressure	22.4 atm.
Freezing Point	-100°C (-148°F)
Odor	Not unpleasant, sweetish smell in small quantities
Boiling Point	72.7°C (163°F)
Vapor Density	2.97 (air = 1.0)
Specific Gravity	0.9338 (water = 1.0)
Solubility in Water @ 20°C.	1.98 wt. %
Flash Point	-5.5°C (22°F) Open cup
Explosive Limits	Lower 2.6%; Upper 13.4% by volume in air

3. Hazardous Properties

- (a) Health Hazards -- No known important health hazards; it is not an active irritant locally and no systemic or chronic effects have been recorded.
- (b) Fire Hazards -- Forms flammable and explosive mixtures with air at temperatures of 22°F and above.

4. Key Points for Safe Handling VAc Monomer

- (a) Keep away from heat, sparks and open flame.
- (b) Electrical equipment should conform to the National Electrical Code Class I, Division II for storage, and Class I, Division I for use.
- (c) Provide adequate ventilation.
- (d) Ground equipment and containers before discharging to reduce danger of ignition from static sparks.
- (e) Totally enclosed systems should be used for processing vinyl acetate as a raw material.
- (f) Must be inhibited with diphenylamine to prevent polymerization in storage equipment and subsequent temperature rise.
- (g) Explosion vents should be used to reduce destructive damage to ducts, mixers, blenders, dryers and similar equipment in which flammable vapors are liable to concentrate.
- (h) Chemical goggles and gloves should be worn when taking samples.
- (i) Frequent inspection of equipment and vessels containing vinyl acetate should be made to detect or prevent leaks. Special precautions listed in Data Sheet SP-75 should be followed in preparing equipment for personnel entry.

5. Specific Hazards at Springfield

- 1. See Section VII, "Polymerization Hazards".
- 2. Although copolymer fire hazards in the rotary dryer have been reduced by recent installation of a "damper and blower", the possibility of an explosion in the dryer, hoppers, silos and bulk cars should be studied.

C. Tetrahydrofuran (THF)

1. Introduction

THF has been in limited use in the PVC area for approximately three years and until recently employed to solvent clean only four reactors.

A new solvent cleaning process is now being started up for extensive use in both 88 Bldg. and 92 Bldg. Quantities up to 15,000 gallons will be stored in the area. Facilities have been installed to solvent clean three reactors per day and to distill approx. 6,000 gallons of PVC laden THF, to remove the PVC.

The only incident experienced at Springfield to date with THF was a feeling of nausea and dizziness by an instrument man while repairing a gauge; during this operation, the man was exposed to excessive concentrations of THF vapor emitting from an open valve on the storage tank.

2. Physical and Chemical Properties

Odor Ethereal
 Color Clear, colorless liquid
 Molecular Weight 72.10
 Boiling Point (1 atm)... 66°C (151°F)
 Freezing Point..... -108.5°C (-163°F)
 Specific Gravity, 20°/4°C 0.888
 Weight, #/gal. at 20°C.. 7.4
 Flash Point (tag closed
 cup)..... -14.5°C (6°F)
 Flammability Limits, %
 by vol. in air at 25°C. 2.0 lower; 11.8 upper
 Ignition Temperature.... 321°C (610°F)
 Miscibility:
 water; esters infinite
 acetones; alcohols;
 chlorinated hydrocarbons

3. Hazardous Properties

(a) Health Hazard

Considered a toxic material with a threshold limit value of 200 ppm; odor readily detected at 50 ppm.

Excessive exposure may cause nausea, dizziness and headache; symptoms disappear quickly on access to fresh air.

THF does not sensitize the skin or cause irritation beyond the normal defatting action of organic solvents.

THF should never be taken internally.

Contact with the eyes should be avoided via protective equipment.

(b) Fire Hazard

THF is about as flammable as acetone and gasoline.

Unstabilized THF forms an organic peroxide when exposed to air; violent decomposition can occur if the peroxide is accumulated.

4. Key Points for Safe Handling

- a. THF storage must be stabilized with .025% butylated hydroxytoluene, BHT, (or 0.10% hydroquinone) to prevent peroxide formation. Samples should be tested regularly to monitor the peroxide level; must be maintained below 0.10% peroxide. Records should be maintained to help monitor the system peroxide level.
- b. THF should be maintained on the basic side to (1) prevent decomposition and THF-peroxide formation and (2) prevent corrosion of steel equipment.
- c. Bulk transfer of THF from tank truck to storage equipment must follow regulations for "flammable liquid" handling.
 - (1) Performed only by qualified personnel.
 - (2) Transfer only in daylight.
 - (3) Motor shut-off during unloading.
 - (4) Use only non-sparking tools.
 - (5) Electrical ground all tanks and lines.
 - (6) Electrical facilities must comply with NEC for Class I, Hazardous Location.
 - (7) Operator must be present during entire transfer operation.
 - (8) Unloading connections must be removed promptly after completion of the transfer.
- d. All storage tanks, pumps and piping should be electrically grounded to discharge static electricity.
- e. All storage tanks must be protected to prevent excessive pressure or vacuum buildup as solvent is transferred. A safety vent should be used on all relief lines.
- f. Welded pipe connections are preferred because ordinary pipe dopes quickly leach out and leaks develop at fittings.
- g. Only recommended materials should be used for gaskets and seals; see duPont Bulletin "Furan Products" FC 5-260.
- h. All THF leaks must be isolated and stopped immediately. The area should be flushed with water and adequate ventilation provided to prevent toxic concentrations from accumulating. In short, handling of THF must be odorless.

- i. THF must be kept away from heat, sparks and open flames.
 - j. All electrical handling equipment must conform to National Electrical Code Class I.
 - k. Design must eliminate any pits or isolated areas where adequate ventilation is not provided.
 - l. Chemical safety goggles and gloves must be worn when sampling THF, repairing equipment, discharging containers or when there is danger of leaks or splashes.
 - m. Air must be excluded from all tanks and reactors when discharging THF into the vessel with sufficient velocity to buildup a static charge -- i.e., rinsing kettle with THF via spray nozzles.
 - n. All equipment, including storage tanks, recovery tank, pipe lines and condensers, should be inspected regularly to insure integrity of design. No temporary facilities, such as flexible lines, hoses, etc. should be substituted for designed equipment.
 - o. The danger of trapped THF in kettle-reflux condensers should be recognized before entry into the equipment.
5. Specific Hazards at Springfield

The potential hazards associated with THF handling are fully recognized by the "Start-up Team" presently engaged in snaking down the equipment installation and demonstrating the "Solvent Cleaning Process". No further comments are necessary in this audit.

D. Isopropyl Percarbonate (A-6)

1. Introduction

The A-6 catalyst has been employed routinely since April 1964 for the production of suspension homopolymer resins in 88 Bldg. This catalyst was a replacement for lauroyl peroxide, which is still used in 92 Bldg. suspension polymerization.

The basic flow of A-6 material through the plant is as follows:

- (a) A-6 crystalline solid is stored in the remote catalyst area on the hill; the material is packed in 10 lb. stainless steel trays; the trays are maintained in contact with dry ice in the original shipping container, an insulated box.
- (b) Daily requirements are transferred from the primary storage to the area storage room.
- (c) A-6 crystalline solid is dissolved in approximately a 1:3 ratio with diethyl maleate (DEM).
- (d) A-6 solution is transported from the storage (and dissolving) room to the kettle floor.
- (e) A-6 solution is transferred to a refrigerated charge tank located at each kettle; quantity of solution is approximately 1 gallon.
- (f) The A-6 solution is pressurized with nitrogen and forced into the reactor at the appropriate time in the polymerization cycle.

The crystalline A-6 is unstable at temperatures above 8°C, the melting point. If stored at room temperature the material will decompose violently, releasing flammable and explosive gases. The A-6 solution is much more stable and temperatures in excess of 50°C are required to attain the auto-decomposition point for the quantity usually handled; violent decomposition will occur at temperatures above 85°C with the expanding gases capable of rupturing a 4,000 psi pressure vessel. With a 2" diameter vent for the holding vessel, the decomposition gases release to the atmosphere without any appreciable pressure developments.

In the brief 4-month period since starting the commercial usage of A-6 catalyst, no hazardous incidents have occurred, except for one when the cover to the primary storage box was lifted by excessive winds one evening. When noted the following day, about half of the dry ice refrigerant had sublimed. Since then, monitoring equipment has been installed and changes in design effected to prevent a similar situation.

For safety purposes, it is mandatory that the regulations, procedures and equipment be utilized properly. Close follow-up is always necessary to avoid complacency and utilization of faulty equipment.

The hazards with A-6 solid, DEM and A-6 solution are defined separately in the sections following.

2. Physical and Chemical Properties of A-6 Solid

Physical State Colorless, crystalline solid
below +8°C
Molecular Weight 206
Melting Point 8 to 10°C
Specific Gravity 1.080 (water = 1.0)
Solubility in water @25°C .04%
Solubility in organic
Solvents..... Miscible with aliphatic and
aromatic hydrocarbon esters,
ethers, chlorinated hydro-
carbons
Heat of Fusion 25 BTU/lb.
Active oxygen content... 7.8%

Stability..... A-6 is highly unstable at ambient conditions; material melts at 8 to 10°C, auto-decomposition occurs at 14-18°C and materials rapidly reach temperatures of 85°C at which point sudden effervescence occurs producing flammable products including isopropyl alcohol, acetone, acetaldehyde, and ethane. Close by sources of ignition constitute an explosion hazard, while complete confinement of the decomposing product can lead to vessel rupture and/or explosion.

Reactivity..... A-6 spontaneously decomposes on contact with mineral acids. Decomposition is accelerated in the presence of amines, aqueous potassium hydroxide or other strong gases.

Friction and Shock Sensitive, but many times less sensitive than benzoyl peroxide. Unusual conditions of heat, friction or shock should be avoided.

3. Hazardous Properties of A-6 Solid

(a) Health Hazard

Material is considered to be slightly toxic. Skin contact with A-6 will cause local damage to the tissue because of the oxidizing power and the low temperature of the material.

(b) Fire & Explosion Hazard

Dangerous if material is permitted to decompose; the decomposition products are flammable and explosive.

4. Key Points for Safe Handling of A-6 Solid

- a. Primary storage of A-6 must be in an isolated area; local insurance inspection bureau and fire authorities should be consulted concerning location -- distance from highways, buildings, etc.
- b. Storage area must be secured from trespassers.
- c. The storage facilities must be adequately vented to remove CO₂ gases evolved by sublimation of the dry ice refrigerant; a partially opened shed with good wind protection is recommended.
- d. The stainless trays in which the A-6 is packed must always be in contact with dry ice; daily inspection and good inventory of dry ice is mandatory.
- e. A warning system - such as a flashing red light - is recommended to monitor the daily inspection and the accidental failure to replace the cover of the insulated A-6 storage box, thus causing rapid loss of dry ice.
- f. Only minimum amounts of A-6 should be stored in the polymerization area; the storage facilities in the polymerization area should be a concrete room designed to contain any explosion and direct decomposition gases to the outside of the building.
- g. The storage facilities must be well ventilated and not contain any form of heat such as steam or hot water pipes, radiators and light bulbs. Naturally all open flames and spark producing tools must be omitted from this area.
- h. The storage areas should not contain any electrical equipment; all moving equipment must be air operated.
- i. The A-6 catalyst should not be subjected to any frictional or grinding operation.
- j. The "transport boxes", used to carry the small daily A-6 requirements from the primary storage area to the plant storage room, must always be accounted for and never left outside the plant storage room -- (which is normally called the "dissolving room").

k. The plant storage room must never be used for any purpose other than that intended; good housekeeping is essential to safe handling.

l. A-6 crystalline solid should not be elevated more than 7 feet off the ground.

m. A-6 spills must be cleaned up immediately.

Large spills should be swept up (use fox tail brush) with Vermiculite, placed in tray containing dry ice and disposed of by spreading it over a sandy area in a safe area.

Small spills should be washed up with soap and water.

5. Specific Hazards at Springfield

None

E. Diethyl Maleate (DEM)

1. Introduction

This material was introduced into the PVC area to serve as a solvent for the A-6 since it is the solution form which makes it practical to charge the A-6 catalyst under precisely controlled condition to the batch reactor.

DEM was selected from tests on series of solvents based on solubility, stability, non-corrosiveness, low toxicity, flammability and the fact that DEM copolymerizes in vinyl chloride reactions thus minimizing undesirable solvent side effects.

The principle hazard with this material is handling; material is a skin sensitizer of moderate to high potency. Three operators have experienced skin rashes while handling this material, requiring 3 to 7 days to clear the local irritation. Since providing better ventilation and enforcing better hygienic rules for handling, no further incidents have occurred.

2. Chemical and Physical Properties

Odor	Noticeable
Color	Colorless, mobile liquid at ambient conditions
Molecular Weight.....	172.2
Boiling Point	225°C
Freezing Point	-11°C
Flash Point	93°C (open cup)
Solubility in Water...	Slight
Vapor Pressure @20°C..	0.07 mm Hg.
Density at 20°C.....	8.9 lbs./gal.
Vapor Density(air=1.0)	5.93

3. Hazardous Properties

- (a) Health Hazard Slightly toxic material with the prime hazard of being a moderate to highly potent skin sensitizer.
- (b) Fire Hazard Only a moderate fire hazard due to low vapor pressure and high flash point

4. Key Points for Safe Handling

- a. Use material only in well ventilated areas; forced air circulation necessary due to high vapor density.
- b. Use chemical goggles (or fire shield) and "oil and chemical resistant" gloves whenever handling this material.
- c. In case of accidental spillage on body, remove clothes and wash skin with soap and water. The exposed eye should be flushed for at least 15 minutes with water followed by immediate medical attention.
- d. Floor spillage should be washed down promptly with water.
- e. Acid impurities in DEM causes attack of steel and brass handling equipment and causes a more disagreeable solvent odor; adherence to quality specification is required.

5. Specific Hazards at Springfield

- a. Closer attention to housekeeping in the dissolving room is necessary to prevent odor in room from reaching a disagreeable level.

Solution: Weekly scrubbing of room should be implemented, together with close monitoring of the daily housekeeping.

D. and

E. A-6 Solution

1. Introduction

The A-6/DEM solution greatly diminishes the stability problem of the catalyst; however, considerable potential hazards still exist. Decomposition, fire and explosion are still possible.

2. Physical and Chemical Properties

Odor	Same as DEM
Color	Colorless, mobile liquid above 0°C
Boiling Point	Decomposes
Freezing Point	Depends on solution concentration; -35°C for 40% solution
Heat of Fusion	25 BTU/lb.

Stability

Tests have shown that decreasing the A-6 solution concentration increases the stability of the system. A 50% solution is maximum allowable based on solution shock sensitivity and difficulty in obtaining further A-6 dissolution.

A 40-50% solution showed the following storage stability.

<u>Temperature</u>	<u>Time</u>	<u>Stability</u>
-10°C	4 mos.	Lost 4% activity in 4 months
- 3°C	2 mos.	No detectable change
+15°C	1 mo.	Lost 2% activity in one week
+40°C	1 gallon of material was raised to 40°C in a 4-gallon pressure vessel; temperature slowly climbed over 1½ hours starting to accelerate at 48°C. From 48°C the decomposition progressed rapidly with a violet decomposition at 80+°C.	

The 28-30% solution routinely used in plant operation is stored at 0 to 5°C; at 10°C an alarm system is activated and at 20°C the material is disposed thus precluding any further problems.

3. Hazardous Properties

(a) Health Hazard -- The solution is considered to be slightly toxic and a highly potent skin sensitizer.

(b) Fire Hazard -- Instability of the solution to temperatures above 20°C is the principle hazard. Material is considered "thermally shock sensitive".

Decomposition products are highly flammable.

4. Key Points to Safe Handling

- a. Only stainless steel equipment should be used to dissolve A-6; metal contamination can reduce the stability of the solution.
- b. Only the specifically designed dissolving tank should be used for solution make-up.
- c. Be sure other drum liquids are not used erroneously in place of DEM; possible error is DAM or antifoams.
- d. Never exceed a 40% weight solution of A-6 in DEM.

- e. Posted steps for dissolution operation must be followed to avoid spillage or overcharging.
- f. Spills should be soaked up immediately with Vermiculite and taken to a disposal area; the floor should be washed down with water.
- g. The disposal area should be a sandy area, restricted to traffic. Gradual decomposition will occur.
- h. The following operating instructions should be posted in the "Dissolving Room".
 - (1) Wear goggles and gloves.
 - (2) Check dry ice level in all storage boxes.
 - (3) Close dissolving tank drain valve.
 - (4) Check current batch formulation data.
 - (5) Tare weigh dissolving tank.
 - (6) Charge DEM to dissolving tank.
 - (7) Tare scale again; check scale accuracy once per shift.
 - (8) Add A-6 carefully - avoid spillage.
 - (9) Carefully move dissolving tank to agitator station.
 - (10) Slowly lower agitator into tank and dissolve A-6.
 - (11) During 10-minute dissolving period, operator should log all pertinent data on batch sheet.
 - (12) Stop agitator, raise slowly.
 - (13) Close dissolving tank cover after mixing; wing nut should be threaded down completely.
 - (14) Immediately transport tank to kettle floor; transfer A-6 solution to correct kettle hold tank.
 - (15) Do not leave A-6 dissolving area until operation is completed.
- i. The A-6 kettle hold tank must be vented at all times except for the brief 5 minutes when the tank is pressurized to charge A-6 solution into the kettle. The 8 inch diameter, two gallon hold tank must be equipped with a full 2 inch vent line extending above the roof line. A fail-safe valve should be installed to automatically open the vent line after an eight-minute period, should the valve be left closed after the charging operation.
- j. The A-6 kettle hold tank must be refrigerated; maintain A-6 solution below 5°C.
- k. The following operating instructions should be posted at the A-6 solution charge panel.

- (1) Wear goggles and gloves.
 - (2) Place dissolving tank in the support ring.
 - (3) Loosen cover of the dissolving tank.
 - (4) Be sure vent valve is open.
 - (5) Drain any liquid from the hold tank.
 - (6) Check brine temperature.
 - (7) Check that bottom valves on hold tanks are closed.
 - (8) Gravity transfer the A-6 solution
 - (9) When batch temperature is at desired range for A-6 charging.
 - (a) drop JTRC set point to 45°C
 - (b) pressurize hold tank.
 - (10) Inject the A-6 solution into the kettle; close drain valve when tank pressure drops to 150 psig.
 - (11) After the injection, depressurize the hold tank.
 - (12) Drain hold tank.
 - (13) Adjust water flush rate to 6 gph.
1. The following emergency procedure should be posted at the A-6 solution control panel.
- (1) Normal A-6 solution Temperature 0 to 5°C
 - (2) Warning temperature (via alarm system) 10°C
 - (3) Drain A-6 solution into container with Vermiculite and dry ice 15°C
 - (4) Allow A-6 solution to decompose in hold tank with 2" vent valve open 30°C or higher
- m. Under no conditions should temporary or other equipment be used to charge A-6 into the kettle.

5. Specific Hazards to Springfield

None

F. Lauroyl Peroxide1. Introduction

This peroxide has been used in suspension polymerization since the initial plant installation. Recently, A-6 catalyst has replaced the lauroyl peroxide in 88 Bldg. operation; the lauroyl peroxide is now used in one building only.

The handling procedure for this material consists of the following:

- a. Prime storage of 100 lb. drums in separate remote building.
- b. Transport of 4 to 8 drums of catalyst daily to the operating area.
- c. Transporting one drum of catalyst at a time to the kettle floor weigh station.
- d. Weighing out batch charge, 20 to 45 lbs., in a carrying pail.
- e. Loading the "delayed catalyst bomb" charge equipment.
- f. Flushing the solid catalyst into the kettle at the correct time in the polymerization cycle.

About a year and a half ago a flash fire was experienced when a small amount of peroxide spilled onto hot pipes below the kettle floor grating. The flame startled the operator who in turn dropped the carrying pail causing the remaining catalyst to spill and catch fire. No injuries or damages resulted.

The cause of the fire was believed to be autoignition of the decomposition gases of lauroyl peroxide. It was estimated, based on laboratory trials, that a 10-15 foot flame could be produced with 25 grams of catalyst. Hence, even very minute spills of catalyst can be dangerous.

2. Physical and Chemical Properties

Formula.....	(C ₁₁ H ₂₃ CO) ₂ O ₂
Molecular Weight	398.6
Appearance	Soft, white granules
Odor	Faint
Taste	None
Melting Point	49-53°C

Solubility (20°C)

Very Soluble (more than 30 grams)*	Benzene, Carbon Disulfide, Carbon Tetrachloride, Toluene, Chloro- benzene, Chloroform, Ethylene Dichloride, Trichloroethylene
Soluble (10-30 grams)*	Acetone, Benzaldehyde, Butyl Acetate, Ethyl Acetate, Methyl Ethyl Ketone
Fairly Soluble (3 to 10 grams)*	Benzyl Acetate, Diethyl Phthalate, Kerosene
Slightly Soluble (0.1 to 3 grams)*	Benzyl Benzoate, n-Butyl Alcohol, Dibutyl Phthalate, Ethyl Alcohol, Iso-Amyl Alcohol, Methyl Alcohol
Insoluble (less than 0.1 grams)*	Water

*per 100 grams of solvent

Stability

<u>Time, Weeks</u>	% Loss of Peroxide Content		
	<u>2°C (35.6°F)</u>	<u>30°C (86°F)</u>	<u>40°C (104°F)</u>
4	0.1	0.1	4.4
8	0.2	0.6	8.1
13	0.7	1.1	27.5
26	1.2	1.6	90.8
39	1.5	2.2	96.6
52	1.5	3.5	--

Half Life Data of L2O2 in Benzene (0.2 moles per liter of solvent)

E, Activation Energy, k cal per mole 30.4

<u>Temperature</u>	<u>Half Life</u>
30°C	900 hrs.
40	220
50	54
60	14
70	3
80	0.8
90	0.2
115	1.0 minutes

3. Hazardous Properties

- (a) Health Hazard -- Although it can cause slight skin and eye irritation, the material presents no significant health hazard.
- (b) Fire Hazard -- The material can be stored safely at room temperature; at elevated temperatures the material is "thermally shock sensitive" with violent decomposition or even explosion occurring.

Although the decomposition products are extremely flammable, the solid burns similar to wax with a soft flame.

4. Key Points to Safe Handling

- a. Material storage must conform to safe practices for peroxide storage; insurance and fire companies should be consulted when designing the equipment.
- b. Keep away from all heat producing equipment: hot pipes, light bulbs, electrical equipment, open flames or sparking tools.
- c. The amount of peroxide in the processing area should be limited to the minimum daily processing requirements.
- d. The containers of peroxide should be stacked in such a way that the water from the sprinkler system will reach and wet them in case of fire.
- e. The peroxide should be stored in the same containers used by the manufacturers for shipping the material.
- f. If the shipping drum is to be re-used for any plant purpose (such as trash collection) extreme care must be used in completely cleaning out any residual peroxide granulars in the drum.
- g. The peroxide should not be subjected to any frictional or grinding operation.
- h. The peroxide should not be added to materials at temperatures exceeding safe tolerances.
- i. Lauroyl peroxide should always be handled in clean, properly designed equipment.
- j. Spills should be removed immediately; the floor area should be washed down completely to remove even trace residues.

- k. The performance of maintenance and repair work on peroxide handling equipment should require a "permit" from supervisory personnel.
- l. Good housekeeping and maintenance of the plant facilities and equipment are essential in all storage and processing areas. A program should be established to accomplish these objectives.
- m. Plant personnel should be thoroughly trained in the emergency procedures required for fires, explosions or accidental spillage.
 - (1) If a fire occurs in the peroxide storage area, the automatic extinguishing system should be allowed to take over and all personnel should leave. Do not approach the fire or attempt to use first aid fire extinguisher; an explosion is a possibility. Use a water spray from a safe distance.
 - (2) Should a fire occur in the vicinity of the peroxide storage area, maintain a cooling water spray over the outside of the containers to guard against overheating.
 - (3) Clean up operations after a fire should not be attempted until all of the peroxide has cooled down completely.

5. Specific Hazards

- a. Spillage of small quantities of lauroyl peroxide is still evident at both the weighing station and at the "delayed catalyst bomb" area. Improved handling methods should be considered and implemented.
- (b) The maintenance of both L_2O_2 and A-6 handling equipment should receive special supervisory attention to avoid spillage. Action to implement this needs definition.

G. Aqua Ammonia1. Introduction

Ammonium hydroxide is used solely in the emulsion polymerization Opalon 440 process. The material is reacted with lauric acid to form an emulsifier, ammonium laurate. The reaction takes place in a 200 gallon tank from which the solution is pumped into the kettle before and during the polymerization cycle.

2. Chemical and Physical Properties

Grades and Strength: Grade A - 29.4% NH₃
 Grade B - 25% NH₃
 Grade C - 15% NH₃
 USP - 27-29% NH₃
 CP - 28% NH₃

Color: Liquid - colorless
 Gas - colorless

Odor: Pungent

Density: 0.8974 (26°Be) for 29.4% NH₃ at 15.5°C

Corrosive: To copper, copper alloys, aluminum alloys and galvanized surfaces.

Affinity for Water: NH₃ gas is very soluble.

Light Sensitive: No.

Explosive Limits of NH₃ Gas: 16 to 25% by volume in air.

Ignition Temp of NH₃ Gas: 651°C (1204°F)

Melting Point of 29.4% NH₃: -72.4°C (-98°F)

Vapor Pressure of Aqua Ammonia:

% NH ₃ , Wt.	Pressure, psia					
	32°F	50°F	80°F	100°F	120°F	140°F
10	0.6	1.1	2.5	4.2	6.7	10.1
15	1.1	1.8	3.9	6.3	9.8	14.9
20	1.7	2.7	6.0	9.7	14.8	22.2
25	2.8	4.8	9.9	15.6	23.0	34.0
30	4.6	7.4	15.2	23.1	34.5	50.3
40	11.2	17.2	32.7	48.4	69.5	97.1

<u>Gaseous Conc.</u> <u>ppm</u>	<u>Effects on Unprotected</u> <u>Worker</u>	<u>Exposure Period</u>
400	Causes irritation of throat	Ordinary not serious for short exposure
700	Causes irritation of eyes	Ordinary not serious for short exposure
1720	Causes convulsive coughing	No exposure permissible; may be fatal after short exposure
5,000-10,000	Causes respiratory spasm, strangulation, asphyxia	No exposure permissible (rapidly fatal)

- (g) Safety showers and eye bubblers should be immediately available at unloading stations and operating areas.
- (h) Protective clothing must be worn when handling, sampling or repairing equipment. Eye protection is a must.
- (i) Operators should be trained not only in operating procedures but also specific first aid action for (1) inhalation, (2) contact with skin and mucous membrane and (3) contact with eyes.
- (j) Contact with eyes, even in minute quantities, is dangerous. Eyes should be irrigated immediately and copiously with water for a minimum of 15 minutes. The eyelid should be held apart during the irrigation to insure contact of water. A physician should be called immediately.

5. Specific Hazards at Springfield

The draft system above the emulsifier tank is marginal; at times NH_3 fumes in the room are detectable and irritating. This problem is compounded by the effect of solution temperatures on the rate of NH_3 vapor generation. The operation should be improved to prevent uncomfortable concentrations of NH_3 .

H. Sodium Hydroxide

1. Introduction

This material is used in only limited quantities in the emulsion polymerization Opalon 440 process. A weak solution, approx. 0.25%, is made by adding flake caustic to water. The liquid caustic soda is pumped into the reactor to stabilize the latex.

No accidents or hazardous incidents have been experienced to date with this operation.

2. Physical and Chemical Properties

a. Anhydrous Form

Color.....	White or light gray
Boiling Point	White heat
Melting Point	310-320°C (590-608°F)
Corrosive.....	Non corrosive to rubber at atmospheric conditions. Slowly corrosive to iron, copper and Monel metal. Destroys living tissue.
Dangerous Reaction...	Yes. Considerable heat is generated when water is added to caustic soda; boiling and spattering of hot caustic solution may result.
Hydroscopic.....	Yes
Deliquescent	Yes

b. Liquid Caustic Soda

Color Water white; occasionally gray

	<u>50% Solution</u>	<u>73% Solution</u>
Boiling Point (760 min)	142 to 148°C	188 to 198°C
Crystallization	+12 to +15°C	+63°C
Solidification	+5°C	+62°C

Flash Point..... None
 Ignition Temp..... None; not combustible

3. Hazardous Properties

a. Health Hazard

Caustic soda is a strong alkali and can cause severe burns. Contact with the eyes, either in solid form or in solution can cause permanent damage.

b. Fire Hazard - None

4. Key Points to Safe Handling

- a. Wherever caustic soda is stored, unloaded, handled, or used, abundant water should be available for emergency use in dissolving and flushing away spilled caustic.
- b. Safety shower and eye bubbler should be located in every area where caustic soda is handled.
- c. Protective clothing must be worn by all operators handling or working near caustic soda.
 - (1) close fitting industrial goggles
 - (2) rubber gloves
 - (3) rubber apron
- d. Operators should be trained for specific first aid action for skin and eyes contact with caustic soda.

5. Specific Hazards

Consideration should be given to substituting a sodium salt for the presently used sodium hydroxide in Opalon 440 process; this would eliminate the handling of this hazardous material.

Should substitution not be possible then improved handling and weighing facilities will be needed; it is not possible to wash down spills in the present storage-weighing room.

I. Calcium Hydroxide

1. Introduction

Lime is slurried in water and charged as an anti-foam to copolymer suspension processes. The normal quantities involved are 30 lbs. of lime added to 10 gallons of water.

This operation has been in existence for approx. 3 years without any hazardous incidents.

2. Physical and Chemical Properties

a. Lime, CaO

Molecular Weight..... 56
Appearance Cubic, colorless crystals
in a finely ground state
Melting Point 2580°C
Boiling Point 2850°C
Reactive..... Upon exposure to dampness
or water, it for calcium
hydroxide. Heat is liberated
during the reaction.

b. Hydrated Lime; Ca(OH)₂

Molecular Weight 74.1
Melting Point -H₂O at 580°C
Boiling Point Decomposes
Density 2.343

3. Hazardous Properties

a. Health

Material has a caustic reaction and therefore is irritating to the eyes, skin and respiratory system.

b. Fire - none

4. Key Points to Safe Handling

- a. Equipment should be designed to minimize spilling and splattering hazards.
- b. Protective equipment must be worn whenever handling lime or hydrated lime. Minimum equipment consists of safety goggles and rubber gloves. Aprons and rubber boots should be worn if spills or splashing dangers exist.

- c. A dust respirator should be used when necessary to prevent inhalation of lime dust.

5. Specific Hazards

Use of protective eye equipment has not been faithfully observed by all operators; additional emphasis on lime protection is needed in this operation.

J. OTHERS1. Trichloroethylene (TCE)

- a. TCE is toxic by inhalation; high concentrations cause narcosis and anesthesia; threshold limit value is 200 ppm.
- b. At high temperatures, TCE decomposes to highly toxic materials (phosgene).
- c. Strong alkalies may react with TCE to form explosive mixture (dichloroacetylene).

Good ventilation and protective equipment is required to safely handle TCE; design of plant equipment should avoid the possibility of combining alkalies with TCE.

2. Glycerine

- a. Glycerine plus asbestos plus heat causes spontaneous combustion.
- b. Glycerine plus peroxides provides a combustible material.

Wherever possible, glycerine should be replaced with a safer lubricant. All leaks must be eliminated in glycerine handling system to prevent dripping onto hot, insulated surfaces.

3. PDR-1, B-1 and B-2

- a. A dust explosion is possible with all three solids.
- b. Spills, when wetted, form an extreme slipping hazard.

Normal handling should be designed to avoid excessive dusting in performing the dissolution operation; good housekeeping is necessary in raw material handling areas.

4. Styrene Monomer (Short-Stop Agent)

- a. Material is a flammable liquid.
 Boiling Point..... 145°C (293°F)
 Flash Point 31°C (closed cup)
 Explosive Limits 1.1 to 6.1% by vol. in air
- b. High vapor concentration irritates eyes and respiratory tract; has an anesthetic acid; threshold limit value is 400 ppm. Material has a disagreeable odor but with good warning properties.

Handling of small quantities of styrene in the area should present no great hazards provided material is handled in safety cans, and spills are avoided.

5. Diallyl Maleate (DAM)

- a. Eye irritation and dermatitis are the chief hazards of this material.

The small quantities in the areas should be moved, sampled, and handled with care to avoid splashing and spillage; protective equipment of safety glasses and gloves should be employed.

6. Potassium and Ammonium Persulfate

- a. Moderately toxic material when inhaled or ingested; also considered an irritant and allergen.
- b. Moderate explosion hazard when exposed to heat or chemical reaction causing temperature to rise to 100°C.
- c. Decomposition products include highly toxic fumes of sulfur oxides.

Store in sprinkler protected area and avoid wet conditions around storage area. Spills should be cleaned up immediately; good housekeeping necessary.

7. Sodium Bisulfite

- a. Moderately toxic material when inhaled or ingested.
- b. When heated to decomposition it emits highly toxic fumes of sulfur oxides.

Store in sprinkler protected area and avoid wet conditions around storage area. Spills should be cleaned up immediately; good housekeeping necessary.

VII. POLYMERIZATION HAZARDS

The following hazards in the polymerization area could cause a leak of flammable materials or produce a source of ignition. All hazards should be eliminated or reduced.

A. Accidental Dumping of Reactors

It is possible for an operator to open the wrong kettle while preparing to transfer a batch from the kettle to the slurry tank. The high pressure in the downstream equipment will immediately cause VCM to escape into the operating area.

It is most probable that the error will be noticed almost immediately and the reactor will be closed again by the operator. However, should the operator be prevented from so doing by leaks or fumes an explosive situation will result.

This problem has been the subject of a PTS project for the past 3 months and it is recommended that the mechanical safe guards under consideration be justified and installed. This will automatically prevent any kettle under pressure from being opened at the dump valve.

B. Glycerine Fires

It has been shown that asbestos insulation saturated with glycerine will undergo spontaneous combustion at temperatures of approximately 100°C.

In the past, there has been 3 fires caused in this manner. One involved the insulation on the kettle itself while the two others were with steam pipe insulation.

Glycerine has been used ever since the PVC reactors were first installed to serve as a lubricant and heat removal fluid from the agitator seals. The inability to completely prevent these seals from leaking glycerine onto the kettle surface and the numerous incidents of glycerine leaks in the process lines makes it necessary to replace this material with a less hazardous liquid.

Again, this problem has been the subject of an active PTS project for the past three months. The effort has been directed at finding a suitable replacement; G-62 is the current candidate.

It is recommended that this project be completed shortly and glycerine be replaced, thus eliminating it from use in the area.

C. Deglassed Areas in Reactors

Years of manually cleaning the PVC glass lined reactors has resulted in glass damage; today considerable areas of the reactor have exposed steel. The corrosion of this steel has been noticeable, especially in the copolymer reactors where the acidic batch and the high temp. process water charge have hastened the attack.

Although not an urgent problem, this condition cannot be allowed to continue indefinitely.

The nickel plating technique has been successfully demonstrated as an economical solution to this problem. It is recommended therefore that a program and time schedule be defined for the upgrading of all PVC reactors.

D. Lauroyl Peroxide Spillage

There is still a noticeable amount of L_2O_2 spillage occurring during the charging of the 92 Bldg. catalyst bombs. Contact of this material with any hot surface (above $65^\circ C$) will result in rapid decomposition and the evolution of very flammable gases, with possible autoignition.

E. Out-of-Control, Probable Set-up Batch

Listed below are the most probable causes for a batch set-up in each process.

Opalon 740

1. Omission of B-1 suspending agent
2. Gross water undercharge
3. Agitator stoppage via power loss
4. Use of antifoam instead of C-1 charge
5. Contaminated G-62

Opalon 600 Series

1. Omission of B-1 or B-2 suspending agent
2. Gross water undercharge
3. Agitator stoppage via power loss
4. Use of antifoam instead of C-1 charge

Opalon 500 series

1. Undercharge or omission of PDR-1 suspending agent
2. Gross water undercharge
3. Agitator stoppage via power loss
4. Aging of PDR-1 solutions at elevated temperatures
5. Iron contamination via RVCM, TCE or water, affecting the suspension system
6. Reflux condenser malfunction

Opalon 400 Series

Reflux condenser malfunction

1. The mischarge or omission of B-1 and B-2 cannot be detected by quick quantitative tests on the kettle floor, as is the case with the PDR-1 suspending agent. Therefore, it is imperative that the probability of operational error be minimized.

It is recommended that the suspension agent charge system be studied and revised to prevent accidental sewerage of the charge; it is of greater urgency now with the closed kettle raw material charging technique, since this eliminates the visual check of flow into the kettle.

2. Two water meters in series are used to accurately gauge the process water charge and therefore no "gross water undercharge" can occur.

There is a remote possibility that the dump valve might be left open during the raw material charging. Since the kettle water charge is no longer dipsticked for volume with the closed kettle charge technique, reliance is placed on the operator to close the dump valve before proceeding.

The use of a "permission switch" should be considered to insure that the dump valve has been closed prior to the start of the raw material charge. It may be possible to combine this device with the work aimed at automatically preventing the dump of a pressurized kettle.

3. Further improvements to prevent uncontrolled agitator stoppage is not warranted since power failures are so few and satisfactory emergency procedures exist.
4. The use of the wrong liquid material for C-1 suspending agent charge can lead to gross problems. The probability of human error has been increased by the large number of drums now necessary for kettle operation; antifoams, G-62, glycerine and C-1 are all handled the same way with unit charges being transferred from a 55-gallon drum to a container.

Compounding the problem area is the limited space for drum shortage with the consequence that no definite location exist for each drum of raw material.

The overall problems of housekeeping, warehouse storage, inventory control, identification of materials, and transporting material should be reviewed and improvements (capital expenditure) requested to upgrade this operation.

5. At present G-62 is filled in 85 Bldg. into reclaimed 55 gallon drums. If a cleaned, reclaimed drum is not used then possible contamination is introduced into the operation.

A better method for control and transporting this raw material is necessary now with the high usage rates in PVC operation.

6. Reflux condenser malfunction does occur but warning signals provide ample time to correct the problem.

VIII. EMERGENCY PROCEDURE

The emergency procedures now in use are concise, precise and up to date. They are posted on each kettle floor and easily available to the operating personnel. These procedures cover the action to be taken for (a) Evacuation (b) Fire (c) Power or Agitator Failure (d) Water Failure (e) Air Failure and (f) Major VCM Spills. In addition, corrective action for any process abnormally is defined in the SDP, with an up to date copy on each kettle floor.

During this audit, the general emergency procedures were reviewed with the objective of developing even faster, simpler and better procedures via nominal equipment installations.

It is recommended that the following changes be made.

A. Styrene Injection System

The present injection systems require a man to carry a one gallon safety can filled with styrene to a kettle, manipulate valves, add styrene to a bomb and then open a kettle valve to drain the styrene into the batch. This system is perfectly adequate when only one kettle is involved in the emergency. For multiple kettle emergency, which exist during any of the above listed problems, the styrene addition procedure requires too much time. Hence, for example the evacuation procedure does not call for styrene injection.

In addition to the time factor, the addition of styrene to a non-agitating (power failure) venting batch via the overhead injection system will not be completely effective. Much of styrene will be volatilized and lost before sufficient mixing is achieved.

The system defined below will eliminate both these deficiencies by instantaneously injecting styrene into all kettles in a building via the sub-liquid step bearing water flush system.

1. Install a 10 gallon pressure vessel to contain styrene; locate immediately behind the control panel at the step bearing rotameter station.
2. Connect the 10 gallon container to the main high pressure water line feeding the manifold; install block valves on the water line and the styrene line.
3. Install a high pressure vessel to serve as a nitrogen reservoir; the nitrogen pressure will be used to force the styrene through the step bearing system against the kettle back pressure.

4. Three fast acting valves with extension handling at the front side of the control panel, would permit rapid (less than 10 seconds) pressurization of the styrene container, water shut-off to the step bearing and styrene addition to the kettles.

B. Full Cold Water to Reactor Jackets

By installing a readily available block valve on the instrument air supply all instruments can be made to "fail safe" thus supplying full cold water to each kettle jacket.

C. Air Failure

By installing a pressure reducer and connecting the available new plant nitrogen supply line in the building to the instrument air supply, a simpler and easier to operate emergency system can be effected. The problems associated with serving nitrogen cylinder and switch over would be eliminated.

D. Emergency Panel

It would be desirable to install the above features together with the presently installed safety devices so that all operations are centralized at one point -- at an emergency control panel.

E. Revised Emergency Procedures

The following revised Emergency Procedures should be introduced with the modifications to the (a) styrene injection system, (b) full cold water system, and (c) air failure system.

1. Evacuation Procedure

Series of Short Blasts Evacuate after carrying out emergency procedure

One Long Blast Evacuate immediately

Procedure after Short Blasts

- a. Stop VCM and VAc pumps.
- b. Close valves before VAc and VAc meters
- c. Put kettles on full cold water by closing air supply valve.
- d. Inject styrene into all kettles.
- e. Proceed immediately to assembly area.

Primary Assembly Area..... Area south of 89 Bldg.
(warehouse)

Secondary Assembly Area Area east of 81 Bldg.

2. Fire

- (a) Attempt to control and extinguish fire with extinguishers in the area. Do not use water on electrical equipment fires.
- (b) Immediately instruct nearest by-stander to turn in the alarm.

 Use Fire Phone - NE corner 88 Bldg.
 - NE corner 85 Bldg.

 Telephone 2771
- (c) Immediately sound Evacuation Alarm

 Short Blast If fire cannot be rapidly extinguished and aid in fire-fighting is required.

 Long Blast Uncertain about the fire controllable or if the fire is in the polymerization area.

3. Power Failure or Agitator Failure

Prompt, positive action must be taken immediately; do not wait to determine if power will be restored shortly.

- (a) Stop all VCM and VAc addition to kettles and close valves.
- (b) Put all kettles on full cold water by closing air supply valve.
- (c) Inject styrene into all kettles, use maximum settings for all rotameters supplying full kettles.
- (d) Vent each operating kettle to the stack for minute in rotating to supply cooling and agitation.
- (e) Monitor kettle pressures; vent high pressure kettles continuously using stack by-pass valve.
- (f) When power is restored:
 - (1) Start all jacket water pumps.
 - (2) Jog kettle agitator for a second; keep repeating until pressure kick subsides, then leave agitator on.
- (g) If at any time a kettle pressure is completely out-of-control sound the Evacuation Alarm and proceed to the assembly area.

4. Water Failure

Prompt positive action defined below must be taken immediately; do not wait to determine if water will be restored shortly.

- a. Immediately stop all VCM and VAc additions to kettles and close valves.
- b. Close instrument air supply valve.
- c. Inject styrene to all kettles; use maximum settings for all rotameters supplying full kettles.
- d. Vent each operating kettle to the stack for one minute in rotation to cool kettle contents.

Simultaneous to the above action, the Foreman and assistants will switch over to auxilliary water supply.

- a. Close main supply

SW corner of 88, 1st floor
SE corner of 92 Warehouse (behind Vredomatic)

- b. Open auxilliary supply

SW corner of 88, 1st Floor
NW corner of 92 Warehouse (behind screen)

5. Air Failure

- a. Close main air supply valve at control panel.
- b. Open nitrogen air supply valve at control panel.

Safety in the Scale-up and Transfer of Chemical Processes

PURPOSE

Many accidents have occurred in the chemical manufacturing industry for lack of complete process information in the operating ranges of plant or pilot plant equipment. Sometimes this has occurred because of inadequate small-scale studies to specify safe operating procedures and appropriate equipment for the larger scale work. Sometimes there simply has not been established a mechanism for checking *all* the critical areas providing background knowledge necessary for safe operation. This Safety Guide has been developed to assist chemical manufacturers in the preparation of such a mechanism.

SCOPE

This Safety Guide covers the following situations:

1. Scale-up within a given laboratory or pilot plant establishment.
2. Scale-up and transfer of a process from pilot plant to a manufacturing plant for commercial or semi-commercial production.

RESPONSIBILITY

The primary responsibility for obtaining necessary process information, including that on safety aspects, lies with laboratory and pilot plant group leaders and their technical people. This responsibility is an integral part of their jobs and cannot be delegated elsewhere. The responsibility begins as soon as work is started on the process, whether on laboratory, pre-pilot, or pilot plant scale. The areas of consideration normally covered are outlined in the check list provided with this Safety Guide. It has been found that a guide of this type is desirable in all stages of process development. It becomes most urgent from the safety aspect when scale-up from one stage to another is planned. It should be borne in mind that certain of the items on the check list may not be critical in small scale operation but highly critical upon scale-up.

When transfer of a product from pilot plant to a production unit is contemplated, review of process data, using the check list as a guide, should be started with the plant people as early as possible before transfer. The plant safety engineer should be included in discussions and should receive full information on process safety. The Manufacturing Department has the responsi-

bility for the safety of its personnel and the protection of its equipment. It must have complete information on which to base a judgment of the hazards of manufacturing any new product.

SAFETY CHECK LIST FOR PROCESS

General Considerations

Review with Safety and Fire Protection engineers and the Manufacturing Department a complete end-to-end narrative of the process with a flow-sheet of the proposed equipment.

Set up a complete material balance on the equipment flow-diagram. Define potential pollution and hygiene problems as well as physical and chemical hazards.

Examine the process and the flow-sheet specifically for the consequences of operator errors and malfunction of equipment. Process procedure and equipment should be thoroughly examined and attempts made to visualize effect of variations in temperature, pressure, sequence of addition of materials, and/or proportion that may result through misoperation or mechanical failure.

Before operating instructions are finalized for the process of any part thereof, it is suggested that a *job safety analysis* be performed. This is a study of the operation, element by element, to identify and to anticipate hazards and to remove them or to neutralize them by specific means.

Detailed Information

Safety factors cannot be isolated. Process safety across a scale-up is an integral part of many inter-related factors including types of equipment, process variables, properties of materials in process, manning, etc. Based on this premise, the following check-list has been designed to provide the background knowledge for anticipating and minimizing hazards.

Product Name

Composition	Structure (s)	Molecular Weight (s)
Physical Properties		
Uses		
Production Volumes and Estimated Costs		
Tentative Specifications		
Storage and Handling Requirements		

Chemistry of Process

Reaction Equations

Reaction Conditions, e.g. time, temperature, pressure, solvent, catalyst, order of addition of materials, etc.

Safe Parameters of such important variables as temperature, pressure and pH.

Process kinetics and thermochemistry

Known side reactions

Possible side reactions

Product stability to heat, light, air, water, storage

Stability of reactants

Raw Materials

Names, structures, compositions

Physical properties

Sources

Tentative specifications

Stability data

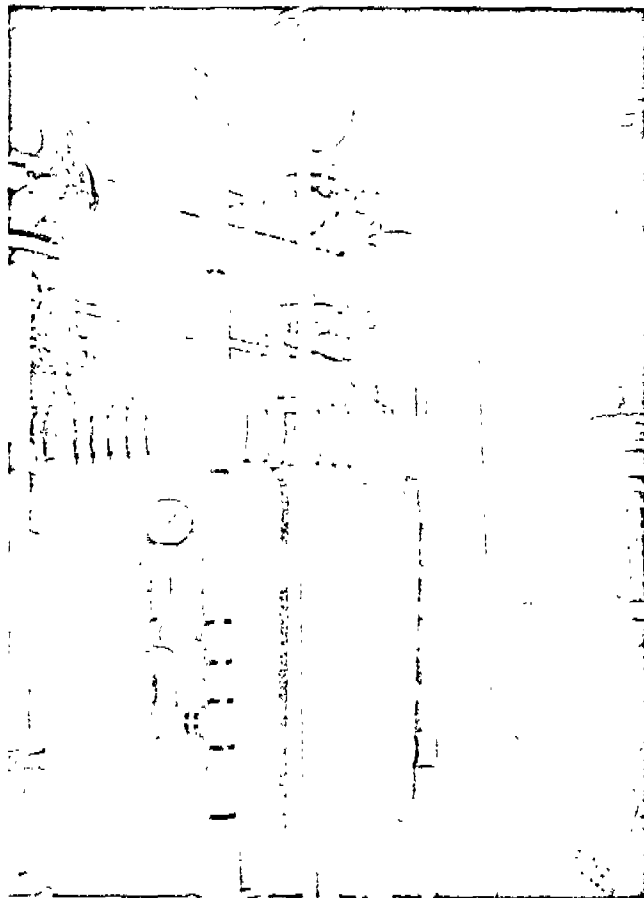
Storage and Handling Requirements

Process Flow Sheets

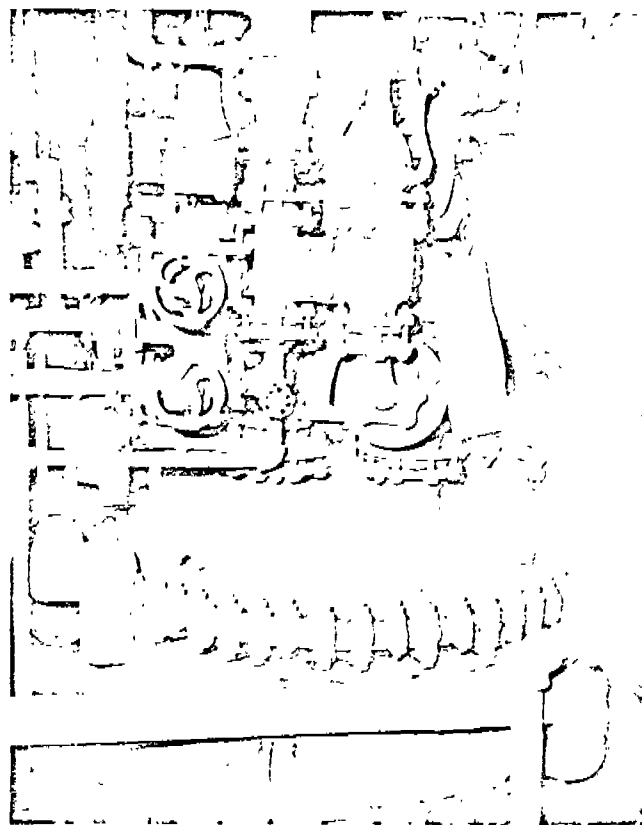
Materials flow streams

Heat duties, and other services

Labor requirements



Select equipment and protection that will provide safe operation.



Operating instructions should include all precautions.

Equipment and Instrumentation

Description

Design data

Materials of construction

Effect of improper control or side reactions on materials

Manufacturers or suppliers

Safety Considerations

Chemical hazards:

Heat effects and rate effects in main reaction and side reactions.

Stability of reactants and products to heat, light, air, water, pH changes, pressure, etc.

Effects of excess or deficiency of one or more reactants.

Possible induction effects, hang-fire reactions.

Estimated decomposition energies of reactants and products.

Flammability characteristics of materials, e.g. flash point, explosive range, auto-ignition temperatures and other pertinent characteristics.

Hazards of drying and grinding.

Equipment hazards:

Effect of power failure, vacuum failure, air leakage, etc.

Fouling of heat transfer surfaces and instrument sensing units.

Health hazards:

Acute and chronic toxicity data on reactants, products and by-products should include oral, dermal, vapor and eye data.

First aid treatments and antidotes for various exposures.

Notification of medical department of work on toxic materials.

Procedures for safe handling of materials.

Procedures for decontamination of toxic or obnoxious materials.

Operating Procedures

Detailed description of recommendations.

Possible effects of deviations from recommended range of operating variables on safety of operation.

Preparation of step-operating chart.

Procedure for discarding unsatisfactory product or intermediates.

Procedure for waste disposal.

Emergency shut-down procedures, or what to do in the event of having to kill a reaction.

Analysis and Process Controls

Analysis of reactants and products

Controls during processing:

Physical methods.

Chemical methods

Final Product

Labeling Requirements

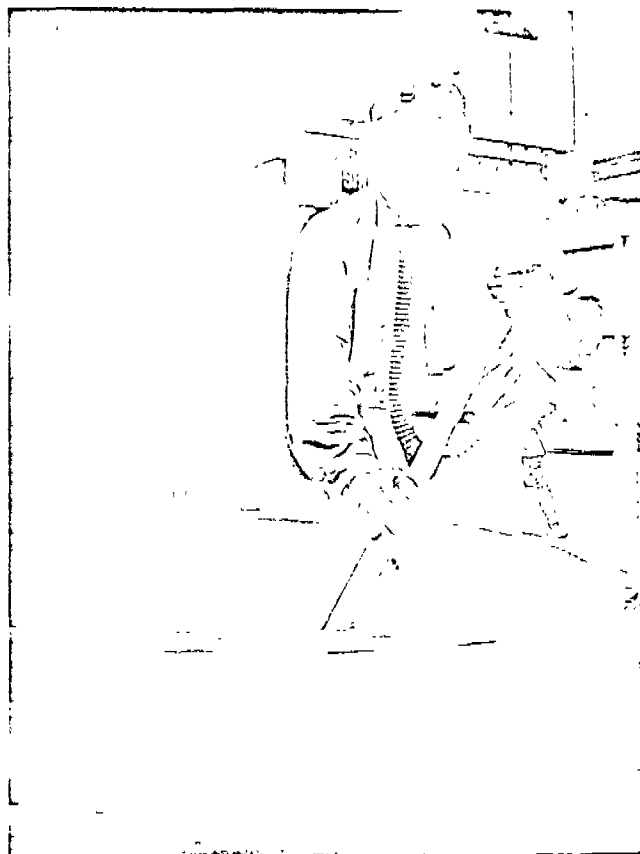
Container Type and Size

Pertinent ICC Regulations

Shelf-life or storage stability

Any special warehousing requirements

Sensitivity to contamination



Make certain that personal protective equipment is specified where required.

FEEDBACK

A process transfer is not complete until a satisfactory operating process or plant is turned over to a manufacturing unit. In the period between the transfer to those doing the scale-up and final transfer to manufacturing, many inadequacies in the original experimental data often show up. It is well to document, with explanation, all of the principal precautions which have been found necessary for the safe operation of the process. Feed back of this information to research and development should result in a continuing improvement of process transfers.

The information and recommendations contained in this publication have been compiled from sources believed to be reliable and to represent the best current opinion on the subject. No warranty, guarantee or representation is made by the Association as to the absolute correctness or sufficiency of any representation contained in this and other Safety Guides and Manuals, and the Manufacturing Chemists' Association assumes no responsibility in connection therewith; nor can it be assumed that all acceptable safety measures are contained in this and other Safety Guides and Manuals, or that other or additional measures may not be required under particular or exceptional conditions or circumstances.

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RSV0023944

Health hazards:

Acute and chronic toxicity data on reactants, products and by-products should include oral, dermal, vapor and eye data.

First aid treatments and antidotes for various exposures.

Notification of medical department of work on toxic materials.

Procedures for safe handling of materials.

Procedures for decontamination of toxic or obnoxious materials.

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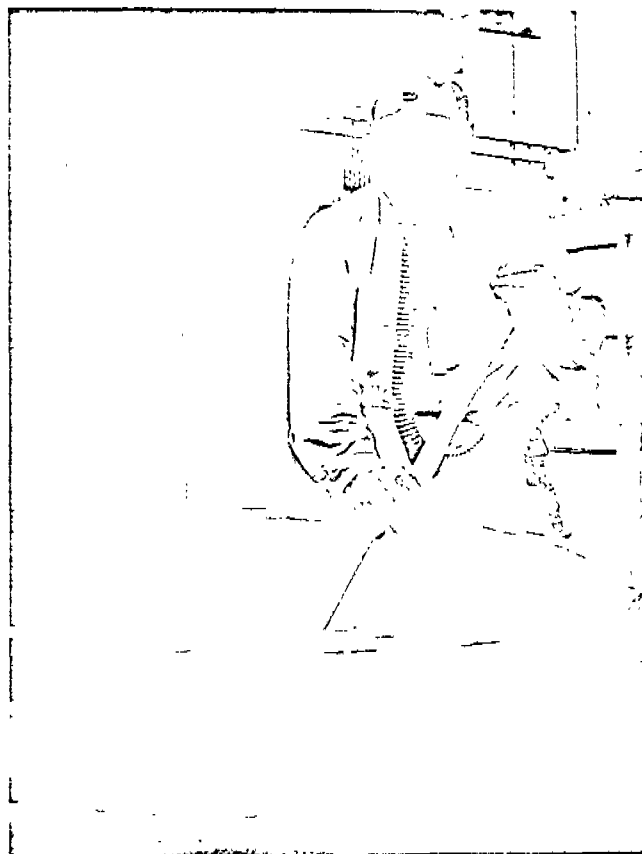
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RSV0023945

PRESENTLY USED RAW MATERIALS

A-2

Material	Container				Prime Hazard	Protective Equip.					
	Form	Tank	Drum	Bag or		1	2	3	4	5	6
				Fiber Drum							
1. VCM	L,V	X			Fire & Explosion	X		X			
2. VAC	L	X			Fire & Explosion	X		X			
3. THF	L	X			Fire & Explosion	X		X			
4. DEM	L		X		Irritation	X		X			
5. A-6	S,L	Special			Fire & Explosion	X		X			
6. L2O2	S		X		Fire & Explosion	X					
7. DAM	L		X		Irritation		X		X		
8. NH4OH	L	X			Eyeburn	X		X			
9. NaOH	S,L	X	X		Eyeburn			X	X	X	
10. Ca(OH)2	S,L	X	X		Eyeburn	X		X			
11. TCE	L	X	X		Irritation	X		X			X
12. Glycerine	L	X	X		Fire	X					
13. PDR-1	S,L	X		X	Slipping	X					X
14. B-1	S,L	X		X	Slipping	X					
15. B-2	S,L	X		X	Slipping	X					
16. Sterox 110	L		X		Slipping	X					
17. Lauryl Alcohol	L		X		Eye Irritation	X					
18. Nopco NXZ	L		X		Slipping	X					
19. Hallco	L		X		Slipping	X					
20. C-1	L		X		Slipping	X					
D-1	S			X	---	X					
G-62	L		X		Slipping	X					
23. Styrene	L		X		Fire & Explosion		X		X		
24. Duponal ME	S,L		X	X	Eye Irritation	X					
25. Duponal WAQM	L	X		X	Eye Irritation	X					
26. Sodium Bisulfite	S,L	X		X	Eye Burns	X					X
27. Sod.Bicarbonate	S,L	X		X	---	X					
28. GMS	S		X		---	X					
29. Pot.Persulfate	S,L		X		Irritant	X			X		
30. Amm.Persulfate	S,L		X		Irritant	X			X		
31. Lauric Acid	S			X	Eye Irritation	X					
32. Normal Octanol	L		X		Irritant		X		X		

CODE: S = Solid
 L = Liquid
 1 = Safety Glasses
 2 = Safety Goggles
 3 = Face Shield
 4 = Rubber Gloves
 5 = Rubber Apron
 6 = Respirator
 7 = Scott Air-Pack (heavy conc.)

RSV0023946

SUSPENSION AREA RAW MATERIALS - MIXING VIA SPILLS

		VCM	VAC	THF	TCE	DAM	DEM	Glycerine	G-62	C-1	A-6	L2O2	D-1	B-1	B-2	PDR-1	Hallco	Sterox	Dytol	Nopco	Lime	Water
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
1.	VCM	X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2.	VAC		X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
3.	THF			X	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
4.	TCE				X	3	3	3	3	3	4	4	3	3	3	3	3	3	3	3	4	3
5.	DAM					X	3	3	3	3	4	4	3	3	3	3	3	3	3	3	3	3
6.	DEM						X	3	3	3	4	4	3	3	3	3	3	3	3	3	3	3
7.	Glycerine							X	2	2	4	4	2	2	2	2	2	2	2	2	2	2
8.	G-62								X	2	4	4	2	2	2	2	2	2	2	2	2	2
9.	C-1									X	4	4	2	2	2	2	2	2	2	2	2	2
10.	A-6										X	4	4	4	4	4	4	4	4	4	4	4
11.	L2O2											X	4	4	4	4	4	4	4	4	4	4
12.	D-1												X	2	2	2	2	2	2	2	2	2
13.	B-1													X	2	2	2	2	2	2	2	2
14.	B-2														X	2	2	2	2	2	2	2
15.	PDR-1															X	2	2	2	3	2	2
16.	Hallco																X	2	2	2	2	2
17.	Sterox																	X	2	2	2	2
18.	Dytol																		X	2	2	2
19.	Nopco																			X	2	2
20.	Lime																				X	4
21.	Water																					X

CODE: 1 = Physical facilities and raw material characteristics such that mixing only possible in kettle.
 2 = No hazard (except possible slipping hazard).
 3 = A potential hazard exists, either separately or together
 4 = A known serious hazard.

COMMENTS: (a) Spillage of A-6 and L2O2 constitutes a serious hazard at all times.
 (b) TCE + Lime --> Dichloroacetylene (explosive)
 (c) Spillage of TCE, DEM or DAM constitutes a potential hazard.
 (d) Lime with water or aqueous material can generate heat resulting in splattering.

EMULSION AREA RAW MATERIALS - MIXING VIA SPILLS

	1. NaOH, flake	2. NH ₄ OH, 29%	3. K ₂ S ₂ O ₈	4. (NH ₄) ₂ S ₂ O ₈	5. NaHSO ₃	6. GMS	7. N-Octanol	8. NaHCO ₃	9. Duponal WAQM	10. Duponal ME	11. Span 20	12. Water	13. Lauric Acid
1. NaOH, Flake	X	4	3	3	3	3	3	3	3	3	3	4	3
2. NH ₄ OH, 29%		X	3	3	3	3	3	3	3	3	3	3	3
3. K ₂ S ₂ O ₈			X	2	3	2	2	2	2	2	2	2	2
4. (NH ₄) ₂ S ₂ O ₈				X	2	2	2	2	2	2	2	2	2
5. NaHSO ₃					X	2	2	2	3	2	2	2	2
6. GMS						X	2	2	2	2	2	2	2
7. N-Octanol							X	2	2	2	2	2	2
8. NaHCO ₃								X	2	2	2	2	2
9. Duponal WAQM									X	2	2	2	2
10. Duponal ME										X	2	2	2
11. Span 20											X	2	2
12. Water												X	2
13. Lauric Acid													X

- CODE: 1. Mixing only possible in kettle.
 2. No hazard (except possibly slipping hazard).
 3. Potential hazard exists, either separately or together.
 4. A known serious hazard.

COMMENTS: (a) Caustic spillage will be serious if in contact with limited amount of water.
 (b) Ammonium Hydroxide spills always a potential hazard.
 (c) The persulfate and bisulfite can be serious if temperature increases and causes decomposition.