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Reactive Chemicals

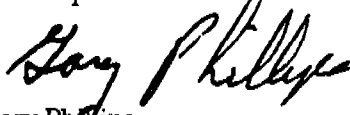
SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF NOVEMBER

December 12, 1995

The following reactive chemicals incidents were reported during the month of November:

- c/A
- A newly completed combination chlorine scrubber and hypochlorite removal tower was involved in an explosion. Hydrogen peroxide (50%) was being used to remove the hypochlorite in the tower. The control system design utilized fail open logic on the peroxide flow so as to avoid an environmental excursion. Unfortunately, when the fail open logic was activated, it allowed the peroxide to build up to high concentrations in the tower. Apparently the caustic in the tower catalyzed the decomposition of the concentrated peroxide, resulting in the explosion. This resulted in a significant loss but no injuries.
 - A VORANOL* reactor experienced a power failure, resulting in a thermal and pressure excursion to 168 °C and 3.5 kg/cm². The product and process were not damaged.
 - During the production of DURSBAN*, a thermal excursion occurred in the reactor which resulted in blowing the frangible pressure relief. The reaction was in the hydrolysis step where Symtet and caustic were being reacted, and an incorrect temperature measurement resulted in a lower than normal reaction temperature. This lower temperature allowed the unreacted caustic level to build up in the reactor. When the reaction started to go, it proceeded at a rate large enough to result in the overloading of the reactor quench system.
 - A small fire occurred in a vent line that was being cleared between the vent condenser and the knock-out pot connected to a reactor producing chloroacetyl chloride. The fire was believed to have been caused by the buildup of pyrophoric material (possibly vinylidene peroxide, chloroacetylenes or other high surface area organics) over time. In the past, this line had been cleaned every three months due to corrosion failure and resulting maintenance on the vent condenser. A process improvement was made by installing a special alloy condenser that did not corrode. This resulted in the vent line not being cleaned for two years, allowing the buildup of more solids in the vent line.
 - A minor thermal excursion was experienced in a reactor producing DOWANOL*. The excursion was caused by a low alcohol flow rate to the reactor. The alcohol flow to the reactor came from an alcohol stripping column that had lost internal reflux, causing the overhead concentration of alcohol to be significantly reduced.
 - Vinylidene chloride samples were discovered to be incompatible and to react with the aluminum septum caps used to close the two ounce sample bottles. A black residue was produced at ambient temperature conditions.


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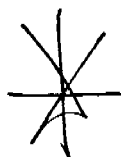
Reactive Chemicals

SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF JULY

August 21, 1995

The following reactive chemicals incidents were reported for the month of July:



- Approximately 15,000 pounds of cell effluent backflowed into the crude PO storage tanks during the process of starting the glycol plant after a 29 day outage. A runaway reaction was averted by plant personnel by promptly removing the caustic layer.
- A couple drums of waste styrene were found to have polymerized in the warehouse and unloading area. The plant is evaluating the addition of inhibitor to the drums as well as looking at ways to limit the inventory of waste styrene in drums.
- A one liter bottle of dried benzyl chloride inhibited with 5 ppm of propylene oxide and containing 100 gm of molecular sieves had been stored on a lab shelf. It was discovered one morning that the bottle cap had blown off, and the contents of the bottle were sprayed on the ceiling and wall. It was discovered that benzyl chloride in the presence of some molecular sieves can decompose to hydrogen chloride.
- A vacuum pump shut down on a vent scrubber connected to a tower, allowing the scrubber liquid containing potassium hydroxide to burp back into the tower overhead, which contained phosphorous oxychloride. The potassium hydroxide and the phosphorous oxychloride reacted causing a pressure spike in the tower. The incident repeated itself, and eventually the system pump plugged up with a gooey liquid later identified as phosphoric acid.

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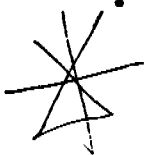
Reactive Chemicals

SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF JUNE

July 13, 1995

The following reactive chemicals incidents were reported during the month of June:



- A large leak in a freon/chlorine heat exchanger resulted in the chlorine concentration in the freon reaching 25% and forcing the shutdown of the system. A large amount of black corrosive oil was produced due to chlorine and iron contamination of the freon compressor lubrication oil. Accelerated tube corrosion was believed to have been caused by inadequate cleaning and drying of the system during maintenance three weeks prior to the incident.
- A high temperature alarm signaled a polymerization reaction occurring in a 10,000 gal styrene recycle tank. The local fire department was called to assist in keeping the tank cool by spraying water on the outside of the tank. The contents of the entire tank eventually solidified and the tank will have to be replaced. The inhibitor had apparently been inadvertently left out of the tank.
- A thermal runaway occurred during the production of a dichloro sulfonamide (a herbicide intermediate). This material is produced in a phosphorous oxychloride solvent which is removed by distillation overhead in a column. Normally, xylene is added to the distillation to help remove the phosphorous oxychloride; but the operator inadvertently added 2,000 pounds of methanol which reacted with the residual solvent, causing a temperature and pressure surge in the column. There was no release of chemicals. Fortunately, most of the phosphorous oxychloride had been distilled and removed from the system.
- A sample from a barge containing ethylene glycol was mistakenly labeled as caustic and sent to the lab for analysis. The lab technical attempted to titrate the sample with nitric acid and realized there was a problem when the sample started to foam.
- Residual butyl ethyl magnesium (BEM) was transferred in an isopar solvent into a tank that was thought to be empty. The tank was not totally clean due to an internal dip leg that had trapped water. The BEM reacted with the water, causing the tank to heat up.
- A pump supplying styrene monomer to two of plants was inadvertently left deadheaded for a long period of time. Fortunately, the primary result was that the magnetically coupled pump was found to have set up with polymer.
- A small spill occurred when cleaning solution that was trapped in leg piping was inadvertently transferred into a hydrocarbon waste tank. The tank pressured up, causing the liquid to spew out an open bleed valve on top of the tank.



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Reactive Chemicals

SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF MAY

June 19, 1995

The following reactive chemicals incidents were reported during the month of May:

- A drum exploded while in the process of being prepared for disposal in a pilot plant area. Several old, rusty unlabeled drums containing unidentified polymer and waste were being emptied by an employee using a hammer to open holes in the lids. The drum was launched an estimated 40 feet into the air and landed 50 feet away, impacting a steam line. The employee was not injured. Ignition of unidentified flammable vapors apparently occurred from a spark generated by the hammer. The employee recalled seeing orange/yellow flames and liquid coming out the bottom of the drum as it was propelled away. Several important learning experiences relative to labeling, housekeeping, waste management and job planning were learned.
- A hydrogen explosion dislodged the covers along the entire length of a chlorine cell series. Excessive pressure apparently developed due to hydrogen not properly venting from the catholyte compartments, causing it to migrate into the anolyte compartment where it violently reacted with chlorine.
- Two parallel pumps in liquid chlorine service failed within a few minutes of each other due to internal chlorine/iron reactions. There was no chlorine released. The cause of the failure was believed to be a combination of pump design and control methods.
- A butadiene storage sphere was discovered to have its relief valves plugged with polymer. The cause of the polymer formation was traced to the installation of a recycle pump that increased the temperature of the butadiene enough that allowed the polymer to form.
- Autoignition of grease occurred in a paper filter cartridge and some internal piping down stream from an air dryer. Difficult to operate, upstream valves had been previously lubricated with a hydrocarbon based lubricant. Part of the corrective action is to use only silicone lubricants for this application. This reactivity issue is similar to other situations where we have oxidizers, such a chlorine or oxygen, in piping and process equipment. Understanding and following good pipe specs is very important.
- A gelation occurred in a reactor of DERAKANE* due to loss of cooling and an overextended process hold step. The failure of a recycle pump was not immediately caught by the control system or operator and manual cooling was initiated too late to avert the gelation.
- A laboratory reaction involving 2-chloro 1-2 ethoxyethyl-benzimidazole and phosphorous oxychloride resulted in a vigorous runaway. The contents of the flask erupted, hitting the top of the hood and splashing on the chemist conducting the reaction. Immediate use of the safety shower averted an injury.

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SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF MAY

June 19, 1995

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CORPORATE SAFETY AND LOSS PREVENTION

Dow

Reactive Chemicals News

Number 288

June 19, 1995

One piece of equipment that we put a tremendous amount of faith in to help prevent reactive chemicals problems is the portable explosion meter. One of our recent reactive chemicals incidents highlighted confusion relative to how these instruments can be used.

There are three or four basic brands of explosion meters found around our plants. All operate on the basis of the sampled gas being oxidized over a catalyst to generate heat that is then detected by a thermal detector. To work properly, the gas must be in a mixture with air. Too low of an oxygen content and the instrument will not register, and too high of an oxygen content and the instrument may become unsafe to use. The instruments can represent an ignition source in high oxygen situations or in situations where the flame arresting device has been removed or is defective. They are all currently designed to be used with flammable gasses in an air atmosphere only. Some of the older MSA brand analyzers required a special flame arrestor to be used on hydrogen, but most of the newer models have arrestors that are designed to handle hydrogen in air. Check your manual for details. The response factor for hydrogen in air is very similar to methane or propane for most analyzers, usually within 20 percent. For accurate readings, it may be necessary to calibrate the analyzer on the actual gas being tested. There apparently existed some confusion in some of the plants regarding the use ability of the meters to detect hydrogen. Some people thought that they were not usable for this. Hydrogen is a difficult gas to find due to it being lighter than air; but the information that we found, including consulting with the manufacturer of the GasTech brand of analyzer, said they do work with fairly accurate response factors.

Other things to be careful of when using explosion meters are:

- The presence of oxidizers other than oxygen in the gas can give errant readings or contaminate the catalyst. Sulfur compounds can deactivate the catalysts.
- The presence of helium, argon, amines or freons can result in incorrect readings.
- Explosion meters should be calibrated at every use, and it is very important to verify that the meter is drawing a sample through the unit.
- The meters should not be used to detect dusts, mists, or wet vapors - only dry gases.
- When in doubt, consult with your analytical group or with the manufacturer of your unit. It might be necessary to sample and test by another means. It should be apparent from this information that the normal portable explosion meter cannot be used for every situation.

Thanks to Jack Motley of the Texas Instrument group for providing much of the information back up for this article.

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Reactive Chemicals

SUMMARY REPORT OF REACTIVE CHEMICALS INCIDENTS

FOR THE MONTH OF MARCH

April 17, 1995

There were seven reactive chemicals accidents/incidents reported for the month of March:

- An incorrect catalyst was used in a styrene polymer reactor, resulting in a runaway reaction and loss of control in a general process styrene train. No property damage resulted, but there was significant off-grade material produced. The wrong catalyst was received as part of a catalyst shipment from a supplier. The wrong catalyst was correctly labeled.
- An explosion and fire resulted when sparks from a welding operation entered an open inspection port in a line between a latex reactor and a condenser. The latex residue in the reactor continued to burn for several minutes following the explosion. The plant was in the process of a maintenance turnaround at the time of the accident.
- A decomposition reaction occurred in the high pressure separator of a polyethylene train. An ethylene vapor line (at approximately 3,500 psig) ruptured due to localized elevated temperatures caused by a "Running Decomp." The decomposition reaction apparently occurred over a period of time and was unusual in that it was not associated with starting up or shutting down the reactor. Significant instrument and equipment damage resulted from the accident, but there were no injuries.
- An activated carbon bed on the ethylene feed to an oxy EDC process autoignited and began to smolder during preparation to remove and replace the bed. Water had not been added prior to opening to prevent the ignition.
- Pyroforic iron sulfide was found in a vessel downstream of an extractive distillation process in a light hydrocarbon plant. Smoke and sparks were observed when the vessel was opened after clearing. The vessel was immediately closed, padded with nitrogen and flooded with water to prevent an accident. This is the first time iron sulfide had been found in this part of the process.
- An incorrectly labeled sample was submitted to a plant laboratory by a contract services company for analysis. The sample was thought to be toluene but was actually isopropanol. When concentrated sulfuric acid was used to wash the sample as part of the analysis, the test tube contents rapidly heated up and blew out into the lab. Upon investigation it was found the sample was caught out of the wrong tank - one that had a similar number to the tank with toluene.
- An epoxy reactor gelled when it was operated on recycle too long during plant problems elsewhere in the plant. Steam was inadvertently left on the reactor for about four hours during the process hold, causing the gelation. Significant costs to clean up the system resulted.

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