THE SOCIETY OF THE PLASTICS INDUSTRY, INCORPORATED

Accident Prevention BULLETIN

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SPECIAL REPORT
February 14, 1969

# VINYL CHLORIDE POLYPEROXIDE EXPLOSION

## Description of Accident

A recent explosion in a vinyl chloride pump seriously injured an operator causing multiple fractures and lacerations of both hands and the subsequent amputation of one finger.

The injured and co-workers were performing routine work cleaning filters and lines in the "recovered" vinyl chloride monomer (RVCM) system adjacent to the polyvinyl chloride (PVC) polymerization plant. Approximately one hour after removing line sections immediately before and after the pump, an explosion occurred inside the idle vented pump causing the head to fracture into 15 to 20 pieces. The injured was standing closest to the pump, approximately 3 feet away. Immediately prior to the explosion, a section of line 6 feet from the pump was vented of vinyl chloride.

The investigation revealed that an unstable material had contaminated the entire RVCM system, including scrubber tanks, compressors, storage tanks, pumps and lines. Analysis of the material showed it to be a vinyl chloride polyperoxide. The dry material is unstable at room temperature and decomposes to carbon monoxide, hydrogen chloride and formaldehyde. The exothermic decomposition is auto-accelerating and the peroxide attains high temperatures generating black fumes. When submerged in water, the polyperoxide is more stable and decomposes slowly. The polyperoxide is soluble and neutralized by 20-30% sodium hydroxide.

There were three abnormal situations in the plant prior to the explosion. The first was the failure of a pressure switch to automatically shut down the RVCM gas compressors at low pressures. The second was the accumulation of RVCM liquid in the storage tanks for 20 days. The third was the use of high acidity level in the vinyl chloride feed stock to the polymerizers.

## Summary of Investigation

Monomer continued to leak from the flange after the explosion, but there was no fire. The area was immediately roped off from traffic and a blanket of water was sprayed over the area. After a while, it was

noticed that a white, gummy, resinous residue was being deposited on the flange by the evaporating RVCM. When sampled and dried with a towel, the material was found to be very shock sensitive, it was possible to detonate the residue with a light hammer blow or by friction. Similar residue was found adhering to the fragments of the pump, and later in the entire RVCM system.

Samples of the residue were analyzed in the Laboratory. The material was identified as a vinyl peroxide, with a composition approximately as follows:

$$\left[-0\text{-}CHCl\text{-}CH_2\text{-}0-\right]_X$$

The peroxide is unstable at room temperature and decomposes to carbon monoxide, hydrogen chloride and formaldehyde. The exothermic decomposition is auto-accelerating and the peroxide attains high temperatures generating black fumes. The material is very shock sensitive. When submerged in water, the material becomes tacky; decomposition subsequently causes the mass to become swollen and porous from the liberated gases. The peroxide is much more stable when submerged in water. It is soluble in a number of solvents, including VCM, and can be dissolved and neutralized with 20-30% sodium hydroxide.

Much of the peroxide in the RVCM system was "impure," being mixed intimately with PVC; this material was less dangerous than the relative pure peroxide deposited at the flange.

The investigation revealed that at least four other PVC producers have experienced problems with vinyl peroxides in RVCM systems. The literature reveals that in the presence of molecular oxygen many of the polymerizable vinyl monomers (such as styrene, methyl methacrylate, vinyl acetate, vinyl chloride, etc.) will rapidly form polyperoxides. The reaction is activated thermally, photochemically, and by radical producing catalysts. As long as oxygen is present, the kinetics favor the formation of peroxides rather than the long chain polymers. Thus, polymerization is inhibited. When the molecular oxygen is consumed, the peroxides formed can decompose and initiate polymerization reactions.

## Accident Causes

1. The explosion in the pump was caused by the ignition of leaking VCM via the decomposing vinyl chloride polyperoxide and compounded by the shock sensitivity of the polyperoxide.

2. The unstable polyperoxide was formed from the excessive concentration of oxygen in the RVCM system introduced by water (scrubber) and probably air leaks (compressors).

3. The RVCM was stored for an unusually long period (20 days) allowing the polyperoxide concentration to attain high levels.

4. The concentrated impurities in the RVCM accelerates the oxidation of vinyl chloride.

## Preventive Measures

1. Recognize the ease of forming dangerous, unstable polyperoxides in RVCM systems by the oxidation of vinyl chloride in the presence of (a) free radical initiators, (b) acetaldehyde, (c) acetylene, (d) ferric chloride or (e) HCl plus $H_2O$ plus steel. At least four PVC producers have experienced problems in RVCM systems.

2. Prevent oxygen from entering the system by:

   a. Pressure and/or vacuum testing equipment periodically.
   b. Minimizing usage of water with dissolved oxygen.
   c. Purging equipment after cleaning with an inert gas.
   d. Monitoring oxygen concentration in gas stream after compressor.

3. Minimize the formation of peroxides by:

   a. Inhibiting the RVCM with an antioxidant.
   b. Not accumulating RVCM in storage tanks.
   c. Monitoring RVCM liquid for peroxide content.

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