VCM Daily Comments

Date: July 28, 1966

cc: W. R. Nisbet
W. H. Slager
R. Rosenberg
J. C. Holland
C. H. Duhon
J. L. Price
T. E. Shirley
P. A. Trost

Department 22

VCM production was 106% of rated capacity. 80,000 gallons of high HCl VCM (2.0 ppm level) was loaded from sphere for shipment to Carbide.

Muriatic Acid Production: 10,400 gallons.

Department 23

EDC production was 94% of rated capacity, with operations normal.

Department 26

O. C. production was 54% of rated capacity. The unit was down 10 hours to inspect Fenwal system, fluidize catalyst bed and to unplug acid scrubber water nozzle.

CBY 1047985

TELEPHONE HUDSON 3 6126

Manufacturing Chemists' Association, Inc.

(FOUNDED 1872)

1825 CONNECTICUT AVENUE, N W.
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August 2, 1966

TO: Safety and Fire Protection Committee
Recipients of April 22, 1966 letter
Mr. M. E. Woodworth, National Fire Protection Association

Subject: "Reactivity" statements in Chemical Safety Data Sheets

Gentlemen:

Enclosed is a breakdown of replies received in response to my letter of April 22 to producers of:

Acetaldehyde
Acetic Anhydride
Acetylene
Acrolein
Acrylonitrile
Butadiene
Butyraldehyde
Methyl and Ethyl Acrylate
Nitrobenzene
Propylene
Styrene
Vinyl Acetate
Vinyl Chloride

The letter requested information on the hazards which may develop because of reaction or polymerization of any of these materials if exposed to fire.

In addition to written commentaries as given in the attached, copies of Shell Chemical Corporation publications on Acrolein and Styrene Monomer were received.

Comments from persons who have not yet responded will be appreciated and will be brought to the attention of the Committee as received.

The Committee Chairman, Mr. A. L. Cobb, has asked me to express

thanks and appreciation to those who have cooperated by providing information which may enable the Committee to make necessary revisions to chemical safety data sheets.

This matter will be included in the agenda for the meeting of the Safety and Fire Protection Committee on September 20, 1966.

Sincerely,

F. G. Stephenson

F. G. Stephenson, Secretary
Safety and Fire Protection Committee

FGS:cm

CBY 3101208

REACTIVITY AL_ POLYMERIZATION QUALITIES \ MATERIALS UNDER FIRE CONDITIONS

Comments by Manufacturers - 1966

ACETALDEHYDE

(a) Material is normally inhibited with acetic acid and expected to be stable under fire conditions. Condensation type reaction could result if flame formed a severe hot spot on tank. Material is very unstable under basic or strong acid conditions. One manufacturer cautions against use of fire water above pH 8 for dilution of tank contents during fire fighting because of possible aldol condensation which could cause a serious explosion.

ACETIC ANHYDRIDE

(a) Acetic anhydride when alone does not tend, under any known circumstances, to polymerize explosively.

ACETYLENE

(a) Acetylene gas can polymerize and/or decompose violently by deflagration or detonation depending on pressure, size and shape of pipe line or vessel. Extreme shock or heating walls of pipe line or vessel adequate for initiation of a decomposition. Acetylene dissolved in solvent usually considered to have the characteristics of the solvent when exposed to fire.

(b) We would expect from the auto ignition of acetylene that runaway reactions leading to rupture of equipment and piping would occur if the temperature of the acetylene reached 500°C. At lower temperatures than this acetylene will polymerize with the evolution of heat which, under the right conditions, could cause the originally mild temperatures, say 300°C., to reach a condition where the entire contents would decompose explosively.

ACRYLONITRILE

(a) No additional hazard. Slow polymerization might occur.

(b) The acrylonitrile which we manufacture is normally inhibited with 35 to 45 ppm of MEHQ; however, under special request we have shipped acrylonitrile con-

taining from 20 to 30 ppm of MEHQ.

Our experience to date with the inhibition of acrylo using 35 to 40 ppm of MEHQ is very good. We have had no problems with acrylonitrile polymerization either during shipment or during storage. Since no fires have occurred in the acrylonitrile storage area, we cannot make comments relative to a fire situation. However, the company standard stability test for acrylonitrile is to subject the inhibited product acrylonitrile to a temperature of 212°F. under an oxygen atmosphere at 100 psig for a period of four hours. If any polymerization occurs in the bomb, the acrylonitrile is considered out of specification.

(c) In our opinion, rupture of the container due to polymerization is a definite potential. At 212°F under a 100 psig O_2 atmosphere (standard O_2 bomb stability test), acrylonitrile polymerizes after 4-6 hours with an instantaneous 100-150 psi pressure increase. Admittedly, this may be an extreme example because of the presence of oxygen. But it does show that the polymerization is rapid with an instantaneous pressure rise. We tried this bomb test a couple of times under an air atmosphere with essentially the same result except the pressure rise was 20-30 psi.

In a tank car with the standard 45 psig safety relief valve setting, the acrylonitrile can heat to about 260°F before the safety valve opens. At these temperatures polymerization would occur quicker and perhaps with greater pressure release than in our tests at 212°F.

In an atmospheric vented storage tank, the acrylonitrile would boil at 168°F and not tend to go above this temperature. Under these conditions, the potential of polymerization would be much less. In fact, under fire conditions, the venting of vapors and potential flash back would be the greatest hazard.

Although not specifically related to fire, we noted that the 1964 edition of the Data Sheet omitted statements concerning the <u>reactivity</u> of acrylonitrile and strong acids. In the earlier editions (for example 1949), they had the statement under 5.2.3 - "Strong acids such as sulfuric and nitric may react vigorously with acrylonitrile. The material should therefore be stored at a safe distance from tanks containing these acids". <u>We suggest the revised Data Sheet include this statement.</u>

(d) We know of no reaction whereby inhibited acrylonitrile will decompose or polymerize to produce violent rupture of the container under fire conditions.

Since uninhibited acrylonitrile is capable of explosive polymerization, there could be concern over the stability of inhibitors under fire conditions or prolonged storage. There was a derailment and fire involving acrylonitrile tank cars at Perdido, Alabama, in May of 1965, in which two jumbo tank cars were wrecked and burned. Despite exposure to fire in this instance the contents did not polymerize.

BUTADIENE

(a) Normally no particular hazard outside of pressure build-up of a liquefied gas. Rate of formation of the dimer is relatively low (1.1%/hr. at 100°C). Large scale evaporation of butadiene would concentrate any peroxides present and possibly cause a detonation as the vessel approached dryness.

(b) When exposed to fire Butadiene has not been found to generate a self-sustaining reaction when exposed to temperatures normally encountered during a fire. In addition, we would not expect any toxic fumes to be evolved other than those normally associated with a combustion of hydrocarbons. Dimerization and polymerization have been known to start at relatively low temperatures and could result in the build-up of polymer in equipment with subsequent failure if this polymer is not removed from time to time. However, this is not associated with rapid reactions which could occur under fire conditions as you suggested in your letter.

(c) In the case of butadiene, we feel there is some possibility of a runaway polymerization in the tank of butadiene exposed to fire. However, the temperature to which this occurs will vary depending upon the presence of antioxidant (inhibitor), peroxides, oxygen, water and iron rust. Normally, a proper pressure relieving system on tanks can be expected to actuate and maintain the contents at a temperature below which polymerization could start.

(d) Butadiene is reactive and will polymerize to polybutadiene when subjected to heat and will form extremely hazardous butadiene peroxides under certain

conditions when contacted with air. Butadiene vessels are known to have ruptured due to internal pressures or explosions. The explosive limits of butadiene in air mixtures are 2.0 percent lower limit and 11.5 percent upper limit. Percentages given are by volume. Butadiene is also flammable.

The following practices or precautions are taken as safeguards against these hazards:

1. Butadiene is stored in coded pressure vessels fitted with adequately sized, dual pressure relief valves. The valve seats are protected from fouling by polybutadiene through the use of rupture discs.

2. Relief valves discharge into a flared vent system.

3. The main storage vessels are located in an isolated diked area.

4. The vessels are spaced according to recommended practice for light hydrocarbons.

5. All butadiene vessels are grounded.

6. Electrical service and equipment is Class I, Group D, explosion proof.

7. A fire water spray or fog system is available for use should the tank farm be endangered.

8. Butadiene is maintained in storage at temperatures below 90°F. Cooling can be accomplished by water spray, mechanical refrigeration, or reflux.

9. All butadiene handling and storage equipment is both pressure and vacuum tight to keep air pickup at a minimum.

10. Oxygen content in the vapor space over butadiene in storage is maintained at low level by reducing the pressure on a regular basis by evacuation.

11. A polymerization inhibitor is added to all butadiene which is not immediately used in polymerization (100 ppm t-butylcatechol is normally added.).

12. Vessels are periodically cleaned of any buildups.

If not already available to you, we suggest that you obtain the booklet, "Recommended Good Practice for Safeguarding Flammable Liquids," issued by Factory Insurance Association.

(e) We believe paragraph 6.2.3 in SD-55 cares for the main point of concern. The data sheet specifically states that polymerization or reaction of these materials is accelerated by heat. This infers that under fire conditions, unless prevention measures or equipment are either designed into the system or conveniently available, pressure rupture of a container is entirely possible. In our experience, for these two materials, this has never happened due to preventive features.

BUTYRALDEHYDE

(a) Butyraldehyde when alone does not tend, under any circumstances, to polymerize explosively.

METHYL AND ETHYL ACRYLATE

(a) Methyl and ethyl acrylate are known to undergo polymerization through the action of heat. There are doubts if this is 'explosive polymerization'.

NITROBENZENE

(a) In answer to the MCA question on reactivity of nitrobenzene exposed to fire, I have never heard nor seen reference to any difficulty of nitrobenzene under such conditions. There are cases where nitrobenzene in combination with some other chemicals, particularly reducing agents, and exposed to temperatures which would not be unusual to reach in a fire, resulted in explosion with rupture of the container.

We have had actual fires involving nitrobenzene in the nigrosine operation with never anything more than simple fire involved. We distill nitrobenzene at 230°C. in a fired still so that the nitrobenzene in the tube is exposed to higher temperatures approximating fire exposure, and have had no adverse consequences.

As far as any closed vessel is concerned on exposure to

fire I would expect that the result would be no different than with any liquid with similar characteristics, in that if not properly vented the vessel would eventually rupture after the contents reached the boiling point.

(b) We know of no reaction whereby nitrobenzene will decompose or polymerize to produce violent rupture of the container under fire conditions. The MCA data sheets appear adequate except that no explosive limits are shown. NFPA 325 shows the lower limit to be 1.8 at 200°F.

PROPYLENE

(a) No particular hazard outside of pressure build-up of a liquefied gas.

(b) We have experienced no polymer problems either during storage or in the shipment of this monomer. Since we have not experienced a fire in the vicinity of the propylene storage tanks we cannot comment on the effects of such occurence. The propylene produced by this company is not inhibited.

(c) Propylene has not been found to generate self-sustaining reaction when exposed to temperatures normally encountered during a fire. In addition, we would not expect any toxic fumes to be evolved other than those normally associated with a combustion of hydrocarbons.

(d) In the case of propylene, there is no appreciable hazard from polymerization under normal industrial use. Runaway polymerization of propylene requires the existence of a liquid phase at high temperatures and correspondingly high pressure that normally would not be possible in a bulk storage or transportation tank.

(e) At times this product is shipped in a 40-45% concentration in a total propane shipment on special customer request. No reaction or polymerization of this product would be anticipated under fire conditions.

STYRENE

(a) Excessive heat would initiate polymerization which would continue to accelerate without adequate cooling. Normal pressure build-up would occur but with the added risk of possible plugged relief valves. It

is estimated that a large majority of the relief valves on styrene cars are normally plugged due to vapor polymerization.

(b) We believe paragraph 5.1.2.2 in the Chemical Safety Data Sheet SD-37 very adequately cares for the main point of concern. It states that polymerization or reaction of this material is accelerated by heat. This infers that under fire conditions, unless prevention methods or equipment are either designed into the system or conveniently available, pressure rupture of a container is entirely possible. In our experience this has never happened due to preventive features.

We believe however that SD-37 could be improved by changing para. 6.2 to read Fire, Explosion and Polymerization Hazards and under a new Polymerization Hazards section, include paras. 5.1.2.2 and 5.1.2.3

VINYL ACETATE

(a) No additional hazard. Has been refluxed at atmospheric pressure for long periods of time without inhibitor.

(b) Vinyl acetate is known to undergo polymerization through the action of heat. There are doubts if this is 'explosive polymerization'.

VINYL CHLORIDE

(a) No additional hazard outside of pressure build-up of a liquefied gas. Long term storage tests of uninhibited monomer have been carried out at 100°C.

(b) Vinyl chloride has been produced by this company for several decades. After discussing the problem of fire hazards in the vinyl chloride storage tanks with a number of the members of our organization who have worked in the vinyl chloride area, I find that to the best of their knowledge we have not experienced a serious fire in the vinyl chloride storage area.

We began testing the storage properties of unhibited vinyl chloride in 1946. Ten years later in 1956 a number of test shipments of uninhibited vinyl chloride were made during the summertime when the vinyl chloride reached temperatures up to 84°F. No polymerization or temperature rise resulting from polymer formation was found during these shipments. In 1958 shipments of uninhibited vinyl chloride to Mexico were studied to

determine whether polymer formation would be encountered during longer shipping periods. No polymer formation was detected. Since 1958 all vinyl chloride shipped and stored by us has been uninhibited. During this period no incident indicating an unsafe practice in the handling of vinyl chloride has arisen as a result of polymer formation. It should be pointed out that the stability of vinyl chloride monomer is dependent upon contaminants in the monomer. Peroxides, in particular, may cause polymerization. The vinyl chloride produced by our process is of a very high degree of purity and, therefore, one would not expect problems with this monomer. Other monomer, depending upon the degree of contamination, could be less stable.

Studies have been conducted on the stability of the vinyl chloride monomer with and without inhibitors. Initiation of polymerization in these tests was accomplished by thermal means, by exposure to light, and by the addition of catalyst. The following results are reported from experiments on the stabilization and storage of vinyl chloride monomer.

In one experiment a tube containing 25 grams of vinyl chloride monomer, 1.25 sq. cm. of rusty iron surface was held at 45°C. in contact with air for twenty-six days, then the temperature was lowered to 40°C. for an additional seventy-four days. No polymerization was detected. In another experiment 25 grams of vinyl chloride containing 1.5 sq. cm. of rusty iron surface under nitrogen atmosphere were held for fifty-two days at 40°C. without polymerization.

The current practice for storage of vinyl chloride is to size the relief valve and vent system such that the vapor produced in the storage tank by fire in the vicinity of the storage tank will be adequately relieved. Current practice is to set the relief valve to relieve at 100 psig. It is estimated that under this pressure the boiling point of the vinyl chloride will be 50.5°C. Since our experimental work on the stability of vinyl chloride was not directed at the specific problem indicated in your letter, the temperatures in the experiments did not include the 50°C. level.

(c) Vinyl chloride monomer at temperatures as high as 100°C (approximately 330 psia vapor pressure) does not polymerize except in the presence of free radical catalysts or actinic radiation. The presence of peroxides in monomer probably

presents the single greatest danger of polymerization in tank cars, tank vehicles, and storage tanks. Oxygen in the vapor space above liquid vinyl chloride monomer or dissolved in the monomer obviously increases the probability of this peroxide formation. The presence of water and/or iron corrosion products accelerates the oxidation process.

We do not consider polymerization of vinyl chloride in tanks under fire conditions to be of any danger provided the following impurity levels in monomer are not exceeded.

Peroxides[1]	0.06 ppm
Water	200 ppm
Iron	0.5 pp,
Oxygen in Vapor Space above Monomer	<0.1 mole percent

Impurity concentrations considerably above these levels may present no danger, and we suspect that somewhat higher levels can be tolerated. We do not know for certain, however. We do not believe that vapor phase polymerization can occur even at very elevated temperatures.

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[1] Total peroxides by colorimetric method based on oxidation of reduced phenolphthalein and calculated as H_2O_2.

(d) If a storage tank or tank car of vinyl chloride monomer was exposed to fire, the vapor pressure would rise in relation to temperature of the monomer. There should be no danger of polymerization, in the absence of oxygen, in the tank before safety relief valves start functioning. As the temperature of the vinyl chloride in the tank rises, the vapor pressure would increase to a point that safety relief valves (or rupture discs) would vent. Due to the proximity of the flames, the ruptured vinyl chloride could burn as fuel, or if mixed with sufficient oxygen from the air, the VC could provide an explosive mixture.