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Notes of NTSB Meeting with William Carroll, PhD, April 5, 2023

National Transportation Safety Board
Washington, D.C. 20594
Office of Railroad, Pipeline and Hazardous Materials Investigations

April 5, 2023

RE: East Palestine, Ohio (NTSB# RRD23MR005)
From: Paul L. Stancil, CHMM, Sr. Hazmat Accident Investigator

Subject: Video conference call with William Carroll, PhD, April 3, 2023

On April 3, 2023, 2:00 p.m. NTSB hazardous materials accident investigators Marc Dougherty and Paul Stancil met in a video conference call with William Carroll, PhD, to discuss the physical and chemical properties of vinyl chloride monomer, and the conditions under which the material would undergo hazardous polymerization reactions as referenced in the Oxy Vinyls LP safety data sheet.

Dr. Carroll worked for Oxy Vinyls for 37 years and he retired in 2015. Oxy has employed Dr. Carroll to consult with them on East Palestine derailment issues. He is also an adjunct professor on the faculty of Indiana University in Bloomington, IN. His biography posted on his company website states that Dr. Carroll received a Ph.D. in organic chemistry from Indiana University in 1978, and he also holds a M.S. from Tulane University, and a B.A. in chemistry and physics from DePauw University. He currently heads his own company, Carroll Applied Science, LLC, and has served as President and Chair of the Board of Directors of the American Chemical Society.[1]

Questioned about the propensity of vinyl chloride monomer to polymerize or undergo violent reactions under certain conditions, Dr. Carroll responded with the following:

- Vinyl chloride does not undergo spontaneous thermally generated polymerization. However, there are some materials that do autopolymerize. Such chemicals tend to have one very weak bond that can be easily thermally cleaved and becomes a diradical that acts as an initiator for polymerization.[2] Structurally, these diradicals have features that stabilize the radical form – vinyl chloride does not have this.
- The reason vinyl chloride does not easily form diradicals is it has a C-C single bond, a C=C double bond, a C-H bond, and a C-Cl bond. The weakest bond is the C-Cl bond. A thermal mechanism would therefore involve cleaving the C-Cl bond, which is equivalent to decomposing PVC.
- The decomposition temperature for VCM is about 550 °C, whereas PVC is thermally destroyed at about 300 °C. Thus, thermal polymerization cannot occur with vinyl chloride.
- A free radical is needed to make vinyl chloride monomer polymerize. Free radicals are typically very reactive materials like peroxycarbonates and peroxyesters (organic peroxide), which at a certain temperature will cleave the double bond and initiate

[1] See: https://billcarroll.org/

[2] Diradicals are an ion or molecule with two unpaired electrons.

polymerization. It takes a continuing amount of free radical to maintain polymerization of VCM – a small amount will not sustain a reaction within a container such as a tank car.

- We asked Dr. Carroll for his opinions about Section 10 of the Oxy Vinyls VCM safety data sheet dated November 30, 2020, which includes the following excerpts: "Polymerizes exothermically in the presence of light, air, oxygen, or catalyst. Explosive or violent polymerization can occur when exposed to air, sunlight, or excessive heat if not properly stabilized. Reacts with incompatible materials and creates strong exothermic reaction…aluminum. Polymerization can occur. Exposure to the following conditions…can cause explosive or violent polymerization…catalytic metals such as …aluminum. Avoid elevated temperatures."
- Dr. Carroll has reviewed the data sheet and has attempted to examine the chemistry behind these statements as well as consulting with other safety professionals. He stated he could not provide any scientific justification for these data sheet caution statements, and he cannot opine why the data sheet contains such statements. He did not provide the content of the SDS and he does not agree with the section on stability and reactivity.
- In his general experience with constructing safety data sheets, dropping caution statements because they are thought to be insignificant hazards is not common practice.
- For example, native aluminum is not thought of typically as a catalytic metal. He already investigated this issue and found a statement in the NIOSH pocket guide that states "avoid contact with copper and aluminum." Dr. Carroll noted there were no chemistry references provided. He believes the SDS is describing the reaction of those metals with hydrochloric acid – not vinyl chloride.
- Vinyl chloride is not an irritant and has very low odor. Dr. Carroll believes the reports of odor in the East Palestine community are more likely connected to the release of acrylates from other tank cars.
- Vinyl chloride is not corrosive. Further, because vinyl chloride had once been used as an anesthetic. He does not believe there is any chemistry that would suggest the material corrodes copper or aluminum regardless of the statements in the SDS.
- Regarding the SDS statement about polymerizing in the presence of light, air, or oxygen, Dr. Carroll referred to a 1992 article on the role of oxygen in the polymerization of vinyl chloride.[3] According to the article, gaseous oxygen will not react with liquid vinyl chloride if it does not contain impurities. In general, oxygen is an inhibitor when trying to polymerize vinyl chloride.
- Questioned for his thoughts on Norfolk Southern's impression that VCM could undergo a runaway polymerization reaction at temperatures of 180 – 185 °F, Dr. Carroll suggested *The PVC Handbook* by Wilkes, Summers, and Daniels (2005) does not have any reference to thermal-only generated polymerization.
- Another recommended reference is: *Kirk-Othmer Encyclopedia of Chemical Technology*, which contains an extensive reference about PVC.
- His reply to the reported temperatures (180 – 185 °F) at which NS believed polymerization would begin to occur is there is no effect to VCM or even to PVC at those temperatures. He stated that during his 37 years in that industry, he never encountered autopolymerization of vinyl chloride.

[3] E. N. Zilberman (1992) The Role of Oxygen in the Polymerization of Vinyl Chloride, Journal of Macromolecular Science, Part C: Polymer Reviews, 32:2, 235-257, DOI: 10.1080/15321799208021426

- Impurities in the VCM, such as oxygen, even at parts-per-million levels, would also inhibit polymerization at the point where it would be used to produce PVC.
- Regarding the combustion byproducts of VCM, Dr. Carroll was able to find only a single journal article that discusses this issue (copy of article provided).[4] The article discusses the amount of phosgene that is generated, being in the 20 to 40 ppm concentration range. However, an optimum air/VCM ratio is required for the production of phosgene.
- Dr. Carroll's opinion about acute hazards from the combustion of VCM is that he is much more concerned about HCl production than phosgene. This is because HCl concentrations in combustion gasses would be about 600 times greater than phosgene. Over time, phosgene will react with water to produce CO_2 and HCl. Therefore, he believes the greatest acute hazard by far would be HCl as an irritant.
- Stoichiometrically, the majority of the yield from combustion of VCM will be HCl. "HCl is where chlorine goes to die in a fire." He said VCM also generates a black sooty smoke plume. Products of VCM combustion include CO, CO_2, and HCl.
- HCl is hydroscopic (draws water to itself), and it is a heavy gas, being not very buoyant in the atmosphere. Dr. Carroll opined that after the thermal push diminished, the vent and burn plume could have bent over with materials and stay close to the ground (subject to wind conditions at the time). Hydrated HCl would tend to be even less buoyant in the atmosphere.
- VCM vs. PVC in a fire… VCM is flammable and will support combustion itself, whereas PVC resin must have a continual source of flame to force it to combust. Momentary ignition of PVC does not support combustion.
- Dr. Carroll assisted in Oxy's response to NTSB about whether VCM, in the presence of aluminum and other metals, can for acetylides (ref. Special Condition B44 in the HMR). Acetylides, or carbides, tend to be generated at very high temperature. For example, calcium carbide is generated at 2,500 °C and is a precursor for making acetylene. In the case of whether VCM could form aluminum carbide, it cannot be produced chemically without the presence of a very strong base (such as lithium and liquid ammonia). The pKa for the first hydrogen is about 24 (the higher the pKa, the less likely the proton (hydrogen ion) is given up), so this reaction is beyond the capability of most common bases (or neutral VCM in normal transportation scenario).
- Regarding the toxicity of VCM or whether it should be considered a PIH/TIH, Dr. Carroll replied that vinyl chloride is not a toxic inhalation hazard. The acute hazard from VCM is asphyxiation in an enclosed space.
- It is not easy to poison someone with vinyl chloride. The material had historically been used as an anesthetic and propellant for hair spray. Vinyl chloride causes a very rare cancer – of the blood vessels of the liver. This was found following a cluster of cases at BF Goodrich in Louisville KY from employees who worked in cleaning reactors. These individuals sustained chronically high exposures over a long period of time.

[4] M. M. O'MARA, L. B. GRIDER & R. L. DANIEL (1971) Combustion Products from Vinyl Chloride Monomer, American Industrial Hygiene Association Journal, 32:3, 153-156, DOI: 10.1080/0002889718506429

- Dr. Carroll agreed to serve as a panelist in the upcoming NTSB investigative hearing to discuss his views on VCM reactivity and polymerization.

PLS (William Carroll Telecon, 4/3/23)