

CONTROL AND RECOVERY OF VINYL CHLORIDE EMISSIONS

The control and recovery of vinyl chloride emissions, when they have been mixed with air, is difficult due to the ease with which vinyl chloride monomer reacts with oxygen to form vinyl chloride polyperoxide. This semi-solid or viscous liquid is unstable and decomposes to carbon dioxide, carbon monoxide, formaldehyde, and hydrogen chloride. The decomposition may be slow or it may proceed with explosive force as is shown in the attached notes from accidents involving this peroxide. The peroxide, too, will catalyze the polymerization of vinyl chloride monomer to polyvinyl chloride. The most comprehensive study of vinyl chloride polyperoxide was reported by Razuvaev, G. A. and Minsker, K. S. in the Journal of General Chemistry, USSR (V. 28, 957-964, 1958). A copy of this report is attached.

The vinyl chloride resin producer must operate his monomer recovery system with care to exclude or minimize the introduction of air into the system. If air is present in the recovered vinyl chloride stream, the following unpleasant or hazardous situations may occur:

1. Polymerization of vinyl chloride monomer to resin is erratic, difficult to control, and usually produces an off-grade product. Loss of polymerization control often leads to venting reactors to the air or vessel failure with fire and explosion hazards.
2. Vinyl chloride polyperoxide will accumulate at some point in the system and suddenly explode as shown in the attached SPI Accident Report.
3. Vinyl chloride polyperoxide will catalyze the polymerization of vinyl chloride monomer to PVC resin in such undesirable places as pumps, tanks, or pipelines, causing plugging and equipment fouling.

The proposed recovery of vinyl chloride from air streams, through use of activated carbon adsorbers, will require intensive study to develop procedures for control or elimination of vinyl chloride polyperoxide. If the polyperoxide is decomposed as fast as it forms on the carbon surface, then the vinyl chloride monomer recovered would be usable with a relatively simple caustic washing unit followed by two distillation columns. The carbon adsorber, in this case, would have to be equipped with adequate cooling to keep it from being ignited by the heat of adsorption and the heat of oxidation of the vinyl chloride. A second, less desirable, situation could

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result if the vinyl chloride polyperoxide catalyzed the polymerization of the vinyl chloride to PVC on the carbon surface. The vinyl chloride would certainly be removed from the air stream and the fouled, activated carbon would have to be replaced with a new charge. The fouled carbon could be safely disposed of as land fill. The third and most serious situation could be the accumulation of the vinyl chloride polyperoxide in the carbon bed over an indefinite period of time until local overheating, shock, or some unknown agent caused it to decompose violently as it often does. The presence of a large amount of carbon in the bed would probably control the decomposition shock wave and only a vigorous fire in the bed would result. Property damage would not be extensive. The collection of vinyl chloride from air streams, using activated carbon, has potential and could be widely used when control of the polyperoxide problem is achieved.

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Attachments

August 8, 1974

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