Vinyl Chloride Peroxide Explosion in a Vinyl Chloride Recovery Plant

B. Terwiesch[a]

[a] Chemische Werke Hüls AG, Marl, West Germany

PLEASE SCROLL DOWN FOR ARTICLE

Vinyl Chloride Peroxide Explosion in a Vinyl Chloride Recovery Plant

B. TERWIESCH

Chemische Werke Hüls AG
D-4370 Marl,
West Germany

INTRODUCTION

The formation of polymer peroxides by the addition of oxygen to unsaturated organic compounds was described for the first time by Staudinger, taking 1,1-diphenyl ethylene peroxide as an example [1]. In the meantime, numerous other polyperoxides have become known, among them the peroxides of acrylonitrile [2], dimethyl butadiene [3], chloroprene [4], methyl methacrylate [5], styrene [6], vinyl acetate [5], and vinyl chloride [7-10]. Because of the great significance of the aforementioned compounds as monomers in the production of plastic materials, the investigations centered on the influence of oxygen on the polymerization behavior of the monomers and on the properties of the polymers.

Little has been known so far about the safety risk involved in handling these monomers with respect to the formation of peroxides. Hendry and co-workers [11] have examined the stability of butadiene polyperoxides, and in the Case Histories of Accidents in the Chemical Industry [12] a reference was found to an explosion of a vinyl chloride pump, the cause of which was stated to have been the thermal decomposition of vinyl chloride polyperoxides. The present paper describes an explosion which occurred at the vinyl chloride recovery plant of Chemische Werke Hüls AG in Marl on December 29, 1978, and also summarizes the results of the investigations made with respect to the cause of the explosion.
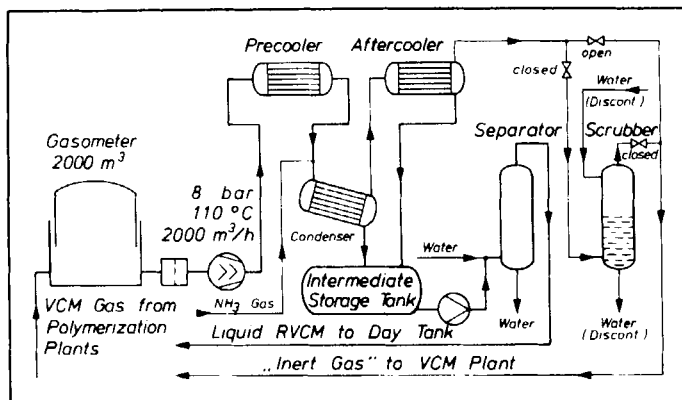
FIG. 1. Modified RVCM process and situation at the time the explosion occurred.

DESCRIPTION OF THE RECOVERY PLANT AND THE EXPLOSION

Figure 1 shows a simplified flow diagram of the plant erected in 1973 with a capacity of 100 metric tons (MT) of recovered VCM/d. The unconverted gaseous VCM from the various polymerization plants was collected in a gas holder, compressed to about 8 bar at a final temperature of 110°C in a two-stage screw compressor with inter-mediate cooling, and then condensed at a temperature of ~30°C. Ammonia was added during condensation for corrosion control. The condensed VCM was continuously scrubbed with water and then re-cycled to the polymerization plant. The uncondensed gases were passed through a batch-type water-fed scrubbing tower and then returned to the VCM plant for further treatment.

One day before the explosion the safety valve of the gas scrubber was found to have a leak. Thereupon, the scrubber was blocked up and vented, and the gas was being returned unscrubbed via a by-pass. The bottom of the tower was heated by steam at 3 bar to prevent freezing. The temperature thus obtained inside the tower ranged from ~20 to 40°C depending on conditions.

On the day of the explosion, it was originally intended to purge with nitrogen and then to drain off the water. However, before this could be done, a severe explosion occurred.

Within a few seconds the entire plant was on fire. The work's fire brigade kept the fire from spreading to the surrounding plants and, apart from this, allowed some 10 MT of VCM contained in the plant at the time of explosion to burn off in a controlled manner. Figure 2 gives an impression of the fire-fighting operations.

FIGURE 2.

Immediately after the explosion, all connecting pipelines of the recovery plant to upstream and downstream plants were closed by quick-action stop valves and no critical situations arose in these plants.

Due to the fact that the plant was operated by remote control, the explosion caused no injuries. On the other hand, the material damage was considerable. As shown in Fig. 3, the outdoor part of the installation was completely destroyed. The total material damage was in the order of magnitude of DM 2 million.

FIRST THOUGHTS ABOUT THE CAUSE OF THE EXPLOSION

Investigations initiated immediately after the explosion leave no doubt that the explosion occurred in the residual gas scrubbing tower. As is obvious from Fig. 3, this equipment suffered the greatest damage. The upper part of the scrubbing tower, designed for pressures of up to 10 bar and made from 10 mm steel sheet, was more or less cleanly
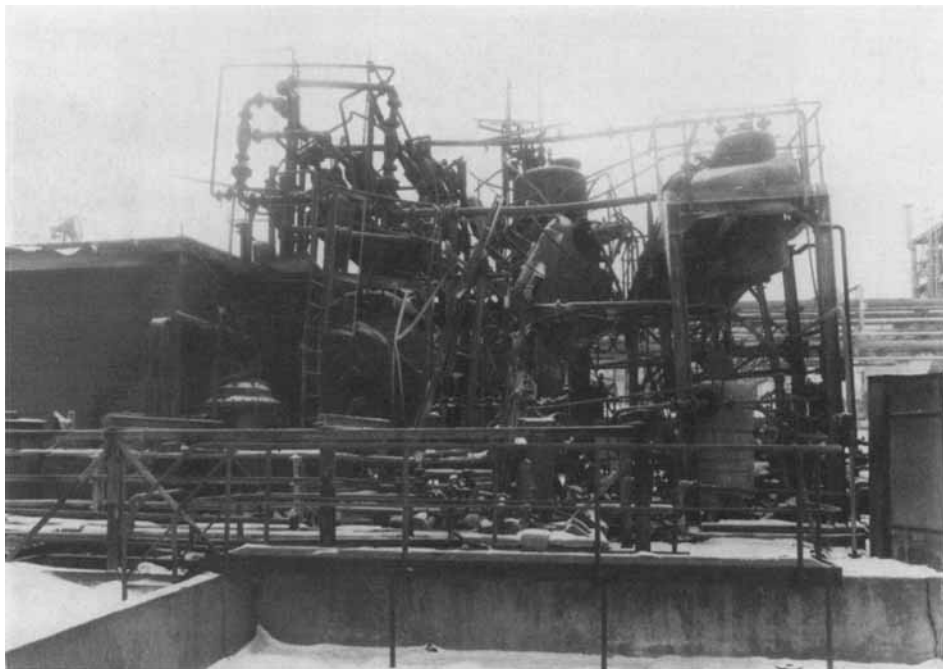
FIGURE 3.

ripped off. As Fig. 4 shows, the lower end plate was torn to shreds, and the adjoining cylindrical jacket was cracked and partly flared out. The legs of the vessel were greatly compressed. These findings indicate the great violence of the explosion.

In seeking the cause of the explosion, the following possibilities were discussed:

(1) Gas explosion of a vinyl chloride/air mixture
(2) Runaway vinyl chloride polymerization
(3) Decomposition of vinyl chloride peroxide

After taking all factors into consideration, Possibilities (1) and (2) were ruled out. In particular, they could not explain the great violence of the explosion. The only possible explanation was the decomposition of vinyl chloride peroxides. However, initially we did not understand how sufficient amounts of vinyl chloride peroxide could have gotten into the scrubbing tower and why they decomposed just at that time.

FIGURE 4.

LITERATURE ON VINYL CHLORIDE PEROXIDES

At the time the explosion occurred we were familiar with literature references concerning the intermediate formation of vinyl chloride peroxides during the polymerization of vinyl chloride in the presence of oxygen [7-9]. The most important results of this work are shown in Fig. 5.

The formation of the peroxide can be regarded as copolymerization of vinyl chloride and oxygen. The degree of polymerization stated ranges from 2 to 7. According to Bauer and Sabel as well as Lederer, the peroxide is thermally decomposed into formaldehyde and formyl chloride, the latter being further decomposed into carbon monoxide and hydrogen chloride. According to Rasuwajew and Minsker, hydrolysis already takes place at low temperatures, followed by further decomposition by one of the reaction routes stated.

Later we came across a paper by Kalinin and co-workers on the stability of vinyl chloride to oxygen at 45°C in the presence of various impurities [10]. Their findings are shown in Table 1. They report that very pure vinyl chloride forms no peroxide at all under the stated
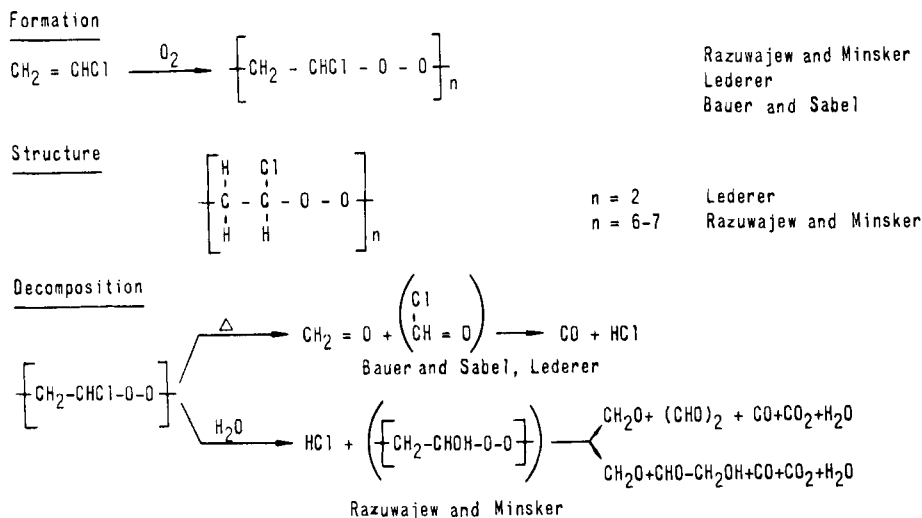
Formation

$$CH_2 = CHCl \xrightarrow{O_2} \left[CH_2 - CHCl - O - O \right]_n$$

Razuwajew and Minsker
Lederer
Bauer and Sabel

Structure

$$\left[\begin{array}{cc} H & Cl \\ C - C - O - O \\ H & H \end{array} \right]_n$$

n = 2   Lederer
n = 6-7   Razuwajew and Minsker

Decomposition

$$\left[CH_2-CHCl-O-O \right]$$

$$\xrightarrow{\Delta} CH_2 = O + \left(\begin{array}{c} Cl \\ CH = O \end{array} \right) \longrightarrow CO + HCl$$

Bauer and Sabel, Lederer

$$\xrightarrow{H_2O} HCl + \left(\left[CH_2-CHOH-O-O \right] \right) \Big\langle \begin{array}{l} CH_2O + (CHO)_2 + CO+CO_2+H_2O \\ CH_2O+CHO-CH_2OH+CO+CO_2+H_2O \end{array}$$

Razuwajew and Minsker

FIG. 5. Literature data on vinyl chloride peroxide.

conditions, and that the addition of HCl and/or H_2O or steel splinters also does not trigger any significant formation of peroxide. If, on the other hand, acetaldehyde, acetylene, $FeCl_3$, or steel splinters in the presence of HCl are added, oxidation of the vinyl chloride, depending on the concentration of the impurities, commences with the formation of peroxides.

In Case Histories of Accidents in the Chemical Industry we finally came across a reference to an explosion in a United States PVC plant which was attributed to the decomposition of vinyl chloride peroxides [12]. The most important facts of this incident are shown in Table 2.

While this reference bore out our view that the explosion in our vinyl chloride recovery plant was also set off by vinyl chloride peroxides, we still did not fully comprehend what had happened. Therefore, a comprehensive investigation program on the formation and the properties of vinyl chloride peroxides was started.

FORMATION OF VINYL CHLORIDE PEROXIDE

Our first objective was the preparation of peroxide for use in chemical and physical investigations. Use was made of a 2-1 steel autoclave in which 400 g of vinyl chloride and 800 g of water were placed and into which oxygen was then introduced up to 10 bar.

TABLE 1. Influence of Impurities in the Oxidation of Vinyl Chloride [10]

VCM quality	Impurities		Peroxide content in VCM % active $O_2 \times 10^3$
	Type	ppm	
Pure	-	-	0
Technical	-	-	0.09-5.0
Pure	Acetaldehyde	25	0.62
"	"	250	1.08
"	"	20,000	6.16
"	Acetylene	2.9	0.38
"	"	29	1.08
"	"	700	6.98
"	Water	300	0.06
"	HCl	1,020	0.00
"	HCl	1,020	0.04
"	$+ H_2O$	20,000	
"	$FeCl_3$	100	2.14
	$+ H_2O$	10,000	
"	$FeCl_3$	100	2.42
	$+ HCl$	200	
	$+ H_2O$	10,000	
"	Fe	Splinters	0.05
"	Fe	Splinters	0.27
	$+ H_2O$	10,000	
"	Fe	Splinters	2.77
	$+ HCl$	200	
	$+ H_2O$	10,000	

After stirring for 2 h at 50°C, we obtained a reproducible amount of ~8 g of peroxide.

For further studies of the conditions of formation, an experimental apparatus was prepared simulating physical and chemical conditions of the destroyed scrubbing tower. According to the mode of operation

TABLE 2. Polyperoxide Explosion in Vinyl Chloride Recovery System [12]

Description	Explosion occurred in a pump for recovered VCM during maintenance work
Causes	1. The explosion in the pump was caused by exothermic decomposition of vinyl polyperoxide
	2. The peroxide was formed from excessive O_2 concentration in the RVCM system
	3. The RVCM was stored unusually long (20 d)
	4. The impurities in the RVCM accelerates the oxidation of VCM
Preventive measures	1. Recognize the ease of formation of peroxides in RVCM systems in the presence of certain impurities
	2. Prevent oxygen from RVCM systems
	3. Inhibit the RVCM with an antioxidant
	4. Do not accumulate RVCM in storage tanks
	5. Monitor RVCM for peroxide content

of the scrubbing tower, gaseous vinyl chloride of different compositions was passed continuously through a liquid phase. Each experiment lasted for about 5 h. After venting the reactor, the reaction mixture in each case was analyzed for vinyl chloride peroxide with an accuracy of ~1 mg. The maximum amount of peroxide obtained amounted to ~1 gram. The most important results were as follows:

Vinyl chloride peroxides were already found to be forming during the oxidation of normal specification vinyl chloride with oxygen in the presence of water. Contrary to our previous opinion, the use of recycled VCM or the addition of specific impurities is not necessary for this purpose.

Temperature has a great effect on peroxide formation. Formation of small amounts of peroxide was found to occur even at -5°C with the peroxide yield greatly increasing at above 35°C and reaching a maximum at ~55°C. At higher temperatures the peroxide level declines because of more rapid decomposition.

The presence of a liquid organic phase seems to be imperative, but this phase need not necessarily be VCM. Formation of peroxide also occurred when using methylene chloride as a liquid phase.

An aqueous phase also seems to be necessary. In the absence of water, no formation of peroxides occurred.

Contrary to original expectations, the formation of vinyl chloride

TABLE 3. Analytical Data and Structure of Vinyl Chloride Peroxide

		Analysis	Theory
Composition:	%C	26.0	25.4
	%H	3.3	3.2
	%O	32.5	34.0
	%Cl	38.0	37.6

Theory column bracketed: $C_2H_3O_2Cl$

Molecular weight (osmotic measurements)	750–1400, average $\approx$ 1000
Structure (IR and NMR analysis)	$+CH_2-CHCl-O-O+_n$
Consistency	White plastic material

peroxide was found to occur not only in the acid range, but also at a pH above 8 (however, in smaller amounts).

The peroxide yield was proportional to the oxygen concentration under otherwise equal conditions as expected for a quasi-first-order reaction.

By adding inhibitors it was possible to suppress peroxide formation altogether. Alkyl phenols proved to be particularly effective.

ANALYSIS AND PROPERTIES OF VINYL CHLORIDE PEROXIDES

Another objective of our work was the improvement of the analytical methods for the detection of vinyl chloride peroxides. We started with iodometrical measurements, but a lot of difficulties were encountered, especially with samples from the production plant which we believe were due to their iron content. Therefore, sodium fluoride was added to mask the iron. But there are still other problems which we do not fully understand. For this reason, we are now checking all our measurements showing a positive result with IR spectroscopy.

In most of the experiments conducted by us, vinyl chloride peroxides of high purity were obtained. Some typical analytical results of these peroxides are shown in Table 3.

These peroxides were sensitive to impact and exhibited great explosive force. In moist condition, their sensitivity to impact was lower, indeed, but gram quantities exploded even under water. Thermal decomposition started at ~40°C, and at temperatures of ~95 to 100°C an explosionlike decomposition occurred.

The peroxides were miscible with vinyl chloride at any ratio. However, in other chlorohydrocarbons and in alcohols, ethers, ketones,

and aromatics the peroxides were also found to be more or less solu-
ble. Solutions of vinyl chloride peroxide in vinyl chloride tended to
form polymers. Approximately 4% of the peroxide was sufficient to
polymerize the VCM into a block. By adding inhibitors such as phenol,
it was possible to suppress polymer formation.

In an aqueous dispersion the peroxide proved largely stable to
chemical attack. It was not hydrolyzed by sodium hydroxide solutions
to any appreciable extent either. However, in the presence of solu-
bilizers, such as alcohol, fast hydrolysis took place.

RECONSTRUCTION OF THE CAUSE OF EXPLOSION

Based on the above investigations, we now assume the following
chronological order of events in the scrubbing tower of our VCM
recovery plant.

Phase 1. As a result of insufficient cooling in the condensers,
additional condensation took place in the scrubbing tower with forma-
tion of a liquid VCM layer.

Phase 2. The oxygen that had concentrated in the residual gases,
possibly supported by further impurities present in the recovered
VCM, gave rise to VC peroxides which initially were dissolved in the
liquid VCM.

Phase 3. After venting of the scrubbing tower, the peroxides
insoluble in water precipitated and were deposited as a tacky mass on
the walls of the tower.

Phase 4. The heat supplied to the tower to prevent freezing was
sufficient to heat the contents to $\sim 40°C$. At this temperature slow
decomposition of the VC peroxide sets in. Poor thermal conduction
in the lumps of peroxide caused build-up of heat leading to another
rise in temperature and finally, at $\sim 100°C$, to the explosionlike
decomposition of the peroxide.

Accordingly, there must have been a coincidence of unusual circum-
stances which not only caused the formation of a sufficient quantity of
peroxides, but also brought about its explosionlike decomposition.
On these grounds it is understandable why similar events did not occur
earlier. Fortunately, it is unlikely that such an incident will happen
again. However, preventive measures should and can be taken.

PREVENTIVE MEASURES

First and foremost in this connection is a strict check on and limita-
tion of the oxygen content. In critical plant areas liable to air leak-
ages, continuous monitoring of the oxygen content is strongly recom-
mended. This applies particularly to VCM recovery plants.

Besides residence time and pH value, the temperature is of par-
ticular importance in the selection of the process parameters.

Particularly critical is the temperature range from 35 to 55° C in which the rate of peroxide formation increases rapidly, whereas thermal decomposition is still found to be so slow as to permit concentration of major amounts of peroxide.

Another protection against peroxide formation is the addition of inhibitors. These inhibitors will, however, have to be selected not only from the viewpoint of preventing peroxide formation but also with an eye to the side effects in PVC production. Here, too, the preferred application appears to be in VCM recovery plants.

Both in the case under review and in the case described in the literature, it has been found that peroxide formation per se does not necessarily lead to an explosion. As a rule, the peroxide will initially be present in a dissolved state in vinyl chloride and safely react to completion by way of polymerization. Sporadically occurring polymerization, especially in VCM recovery plants, is a sign of this. The position becomes critical if for some reason or other, e.g., shutdown of a plant, solid peroxide is separated out. The danger of an explosion being triggered off mechanically is then accompanied by the risk of autoaccelerated thermal decomposition. Special attention should be devoted to such phenomena. In such a case one should not rely on purging with an aqueous sodium hydroxide solution since the peroxide will not be attacked sufficiently. It would be preferable to use alcoholic hydroxide solutions or organic bases which will dissolve the peroxide and thus not only accelerate the decomposition decisively, but also prevent an explosion from being triggered off by impact.

ANALYTICAL METHODS

1. Iodometric Determination of Traces of Active Oxygen in Vinyl Chloride

With the complete exclusion of air, 50 mL of glacial acetic acid and a certain amount (~100 g) of liquid vinyl chloride are placed in an Erlenmeyer flask.

In order to mask traces of ferric salts, ~0.5 g of sodium fluoride is added.

Subsequently, 10 mL of 10% methanolic sodium iodide is added with a pipette. The mixture is protected against the action of light. Using a reflux condenser fitted with a Bunsen valve, the vinyl chloride is evaporated at room temperature. To remove residual vinyl chloride, the mixture is then heated in a water bath of 35°C for about 15 min. Together with 100 mL of distilled water, the content is filled into a beaker and titrated potentiographically with 0.01 standard sodium thiosulfate solution using a platinum calomel electrode.

In the same manner, a blank test is carried out without a weighed sample (maximum consumption: 0.2 mL 0.01 standard $Na_2S_2O_3$ solution).

All tests must be conducted under an inert gas atmosphere (CO_2 or N_2).

Limit of detection: 0.5 mg of active oxygen/kg VC.

2. Infrared Spectroscopic Determination of Vinyl Chloride Peroxides

At wave numbers of 750, 890, 910, 1010, 1080, 1230, 1270, and 1335 cm^{-1}, vinyl chloride peroxides show typical absorption bands which may be used in semiquantitative analyses. For the preparation of the samples, extraction with methylene chloride has been found to be practical. The solution thus obtained is concentrated in a rotational evaporator at a pressure of P_{abs} 0.1 bar.

The spectrum is obtained either from the solution (absorbing layer 0.1-0.5 mm) or from the evaporation residue. A quantitative analysis is made by comparison with a standard spectrum, preferably at wave numbers of 1010 and 1080 cm^{-1}.

ACKNOWLEDGMENT

REFERENCES

[1]   H. Staudinger, Chem. Ber., 58, 1075 (1925).
[2]   K. C. Smeltz and E. Dyer, J. Am. Chem. Soc., 74, 623 (1952).
[3]   W. Kern and A. Stallmann, Makromol. Chem., 7, 199 (1951).
[4]   W. Kern, H. Jockusch, and A. Wolfram, Ibid., 3, 223 (1949).
[5]   C. E. Barnes, R. M. Elofson, and G. D. Jones, J. Am. Chem. Soc., 72, 210 (1950).
[6]   F. A. Bovey and I. M. Kolthoff, Ibid., 69, 2143 (1947).
[7]   G. A. Razuwajew and K. S. Minsker, J. Allgem. Chem. USSR, 28, 983 (1958).
[8]   M. Lederer, Angew. Chem., 71, 162 (1959).
[9]   J. Bauer and A. Sabel, Angew. Makromol. Chem., 47, 15 (1976).
[10] A. I. Kalinin et al., Chem. Ind., 1, 27 (1966).
[11] D. G. Hendry et al., Ind. Eng. Chem., Prod. Res. Dev., 7, 145 (1968).
[12] Case Histories of Accidents in the Chemical Industry, 3, 142 (1970).