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VINYL CHLORIDE AS ~~AN AEROSOL~~ PROPELLANT for aerosols

Since AA-1154, Evaluation of Vinyl Chloride as a Propellant for Aerosols was written, new information has come to light which modifies the outlook for vinyl chloride in aerosols. Experiments by Biochem which show much higher toxicity than heretofore realized, and the serious competition offered by propellant mixtures containing petroleum hydrocarbons are the most important factors. The possible reaction of vinyl chloride with components of perfumes, the difficulty of patenting the mixture of vinyl chloride-Propellant 11-Propellant 12, the competition this mixture would offer to Chlorothene and methylene chloride, and the evidence of corrosivity of vinyl chloride also are discouraging. In view of all the above factors, the conclusion is reached that development work on vinyl chloride as an aerosol propellant should be discontinued.

Sprays: aerosol, propellant for, vinyl chloride

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INTRODUCTION:

Vinyl chloride has been investigated entensively as a propellant for aerosols. In AA-1001, the early work on mixtures of vinyl chloride and propane (Propellant D) for aerosol paints was reported. This study covered vapor pressure investigations, possibility of polymerization in aerosol cans, flammability and market potential. In AA-1154, the flammability of vinyl chloride and its mixtures with fluorinated propellants were investigated more thoroughly. The market potentials were modified in light of discoveries concerning the flammability of mixtures of vinyl chloride with fluorinated propellants.

Following publication of this report the decision was made to discuss the matter with a consultant to obtain advice on proceeding further with the development. Dr. Winston H. Reed was selected because of his previous work with Propellant A, a blend of butane with the fluorinated hydrocarbon propellants. The consultation session verified some of our findings, but raised new points which have bearing on the potential for vinyl chloride in aerosols.

This report will review the data developed to date and summarize the reasons why the writer feels that development work on this product should be stopped.

DISCUSSION:

A. Toxicity

The established safe concentration of vinyl chloride for an eight-hour working day exposure by human beings is 500 ppm. This value was based on work done a number of years ago and had not been thoroughly checked out by Dow. In view of the fact that the proposed use for vinyl chloride represents the first time the consuming public would come into contact with the monomer of vinyl chloride, the Biochemistry Research Department instituted studies of the vapor toxicity of vinyl chloride.

Shortly after the work began, it became apparent that the 500 ppm level was having definite detrimental effect on the animals. Now that the first stage of the program is complete, it has been found that some detrimental effect is shown at a 100 ppm level after six months on some animals. This was the lowest level tested, so it will be necessary to repeat the experiment to determine the actual safe working level. This level will have to be set somewhere below 100 ppm, however. Methyl chloride, which has an MAC of 100 ppm has never been widely used in aerosols. The toxicity of methyl chloride is frequently cited as a reason for its limited application.

Aerosol packages are filled by two methods. In the cold fill technique the concentrate is chilled and added to the can. The cold propellant is added next and finally a valve is placed on top and crimped. Between the time the propellant is added and the valve is crimped, the propellant evaporates into the working area. This is not serious while the line is in operation, for the cans are exposed for only a few seconds before sealing. When the line stops, however, the cans may be left open for prolonged periods. Propellant losses normally run from 2 - 5% but some fillers report that 10 - 12% of their purchased propellant is lost.

In the pressure filling technique, the concentrate is added warm. The valve is attached next and the final operation is the "gassing" of the propellant through the valve. This addition of propellant is slower and consequently, pressure filling lines normally produce fewer cans per minute than cold filling lines. In pressure filling, it is necessary to remove as much of the air as possible from the can before the propellant is added. If this air is not removed, the pressure in the finished aerosol package may be excessive. This is done in some lines by squirting a small amount of propellant into the can before the valve is crimped. This propellant evaporates and displaces the majority of the air. The lost propellant is low in this operation, but still some of the material does evaporate into the working space and represents a toxicity hazard.

In Europe where vinyl chloride is used extensively, the majority of filling lines use the pressure fill technique. This method reduces the fire hazard during filling and also diminishes the toxicity problem. In the U.S.A., the majority of lines are cold fill lines. As a result the fire hazard of flammable propellants has sharply limited their use. While it would be possible to install adequate ventilation to control vapor concentrations, this would represent an additional expense to the filler. As will be shown later, the filler can obtain similar cost savings without adding such equipment by using other propellant modifications.

The M.A.C. concentration has little direct connection with the hazard to the aerosol user, since no aerosol is sold at present which would expose the user to fumes from the propellant for periods of over a few minutes. The aerosol loaders are not technically qualified to understand the intricacies of toxicity and would probably conclude that a low M.A.C. means an increase consumer hazard. They would be leary of utilizing a product with a low value. The fluorinated propellants have an M.A.C. of 1,000 and even this high value is not a real maximum. It could have not been set higher on the basis of toxicological data.

The low M.A.C. value for vinyl chloride would make it hazardous during filling operations and would be a serious sales hurdle in the minds of aerosol loaders. Since the level will have to be below 100 ppm, further work on vinyl chloride seems unjustified.

B. Competition From Other Products

In 1956 the development of Propellant A was announced. This was a mixture of isobutane, Propellant 11 and Propellant 12. Experiments indicated that if the concentration of isobutane did not exceed 10% in such a mixture, the combination was not flammable or explosive. No further information has been seen in the literature and it was assumed that the product had encountered difficulties, possibly from the odor often associated with petroleum hydrocarbons.

Dr. Reed indicated that difficulties (he did not indicate the nature of these problems) had delayed the further promotion of Propellant A, but that he expected these to be cleared up shortly and felt that the product would be actively promoted in the near future.

Since isobutane sells for $0.03 per pound, the cost savings experienced by replacing 10% of the Propellant 11-Propellant 12 mix (which sells for approximately $0.23 per pound) would be nearly as great as the savings obtained by replacing 25% of the Propellant 11-Propellant 12 mix with vinyl chloride which sells for $0.12 per pound.

Since Dow does not currently produce Propellant 11 or Propellant 12, it would be necessary for us to interest one of the current producers in buying the vinyl chloride from us and mixing. Few aerosol loaders are equipped to mix propellants or to handle as flammable a material as pure vinyl chloride. Those few that are so equipped would probably prefer to purchase the less expensive petroleum hydrocarbon propellants.

One of the obstacles to the development of Propellant A has been the lack of interest on the part of the propellant producers in promoting the sale of the mixture. Dr. Reed indicated that they object to purchasing tank car quantities of isobutane, since only a small amount is used in each tank car of the Propellant A sold. The rest must be carried in inventory. The following example shows that the problem would also apply to vinyl chloride.

8,000 gal. of Isobutane weigh 32,000 lbs.
8,000 gal. of Propellant A requires 8,000 lbs. of Isobutane

The sale of four tank cars of Propellant A would be required to move one tank car of isobutane.

8,000 gal. of vinyl chloride weigh 60,000 lbs.
8,000 gal. of a 25% vinyl chloride
75% Propellant 11-Propellant 12 mix would require
20,000 lbs. of vinyl chloride.

The sale of three tank cars of the vinyl chloride mixture would be required to move one tank car of vinyl chloride.

The tank car of isobutane would cost only about $900.00, while the tank car of vinyl chloride would cost $7,200.00. Any objections that propellant manufacturers would have against isobutane would be even more vigorous in regard to vinyl chloride. Further, since more of the manufacturers product would be replaced (25% versus 10%), the interest of the propellant manufacturers would be reduced even more.

The competition offered by Propellant A would appear to be more serious than previously anticipated. Any effort to promote a vinyl chloride mixture would probably meet with increased activity by the holders of rights to Propellant A to promote their products.

Dr. Reed indicated that over 5,000,000 cans of various products (including Bridgeports Brass's "Goodaire" room deodorant) have been made and sold using Propellant A. The manufacturing, storage and marketing information compiled on Propellant A would be substantial. Since vinyl chloride is a new material in this country, it would require time to develop similar background information. During this period, sales would be more difficult since fillers desire a great deal of data on valve leakage, effect on filling machinery, etc.

C. Reactivity

In AA-1001, the possibility of polymerization of vinyl chloride in the aerosol can was investigated. No evidence was found of reaction in the test performed, even though known polymerization catalysts were included.

Dr. Reed raised a question concerning the possibility of reaction between vinyl chloride and the perfumes used in various aerosols. Perfumes are a complex mixture of various ingredients and the likelihood of reaction with some of these over a period of time is good. Such reactions would probably change the nature of the odor.

In the area of hair sprays, the perfume used in various products is extremely important. The companies selling hair sprays have been reluctant to modify their perfume for fear of unfavorable consumer relation. This would appear to be a relatively minor point, but considerable sales resistance to Chlorothene in hair sprays has been encountered because of its odor. Since it would be almost impossible to show that there is no reaction between vinyl chloride and the perfume, this argument might be a difficult one to overcome if any customers raised it. The potential market for vinyl chloride of 30,000,000 pounds per year included 10,000,000 pounds per year for hair sprays which would now appear more difficult to obtain.

D. Patentability

The Patent Department has been consulted concerning the prospect for obtaining patents on the use of vinyl chloride in aerosols. They have indicated that the cost savings feature of mixtures of vinyl chloride with the fluorinated propellants would probably not be sufficient to base a patent on, particularly since the savings would not be much greater than that obtained from Propellant A. A much stronger position would be possible if the mixture containing vinyl chloride possessed some unique features which mixtures lacking vinyl chloride did not have. To date, the higher solvency power of vinyl chloride as compared with Propellant 11 and Propellant 12 is the only unique property uncovered and the magnitude of this effect is not great. It is possible that further study might uncover such unique features, but in view of the other factors mentioned above, such work does not seem justified.

E. Adverse Effect on Other Dow Products

The cost savings realized from the use of a 25% vinyl chloride 75% Propellant 11-Propellant 12 mixture are almost identical with those obtained from using Chlorothene or methylene chloride as a 50% replacement for Propellant 11. It is difficult to estimate how much

Chlorothene or methylene chloride business would be lost if vinyl chloride were actively promoted, but since all three products are potentially useful in the same kind of aerosol products, the effect would probably be significant. Since a large amount of information is available on Chlorothene and since this is an exclusive Dow product, it would seem wise to devote anyadditional effort in the aerosol area to promoting its sale rather than to develop a competitive material.

F. Corrosivity of Vinyl Chloride

The literature indicates that vinyl chloride is less subject to hydrolysis than Propellant 11 or Propellant 12. No corrosion studies have been instituted here to check this information, however, some data obtained as a result of another study would indicate that this is open to question.

A series of aerosol cans were partially filled with various solvents used in pressurized paints. Half of the cans were pressurized with Propellant 12 and half with Propellant D. Pressure readings were taken to determine if significant difference existed when Propellant 12 was replaced with Propellant D. No marked differences were noted and the cans were placed in room temperature storage for six months. When these cans were opened after six months marked corrosion was observed in the cans containing methyl ethyl ketone and methyl isobutyl ketone which also contained Propellant D. No corrosion occurred with the cans containing Propellant 12 with these solvents. Since the solvent in both cases was identical in all respects, the increased corrosion must have been due to the presence of the Propellant D. No noticeable corrosion was observed in cans containing butanol, ethanol, butyl acetate, acetone, VM&P solvent, or toluene but a definite discoloration of the nylon valve body was seen in nearly every can containing Propellant D but none was seen in the cans with Propellant 12. It is not known how serious this discoloration is since no valve leakage data was obtained. The presence of corrosion and valve discoloration, however, would indicate that extensive testing studies would be required before vinyl chloride could be marketed.

CONCLUSIONS:

1. A lower M.A.C. for vinyl chloride, which appears inevitable on the basis of recent experiments, would make its sale as an aerosol propellant much more difficult.
2. Propellant A, which contains isobutane, appears to possess many of the desirable features of a vinyl chloride-Propellant 11-Propellant 12 mixture without some of its disadvantages. Extensive promotion of Propellant A is anticipated in the near future.
3. The possibility of reaction between vinyl chloride and perfumes would reduce its acceptance in aerosol hair sprays, a major projected market.
4. The patent picture on vinyl chloride does not appear bright unless some unique benefit could be found for the material.
5. Competition with other Dow materials reduces the appeal of vinyl chloride.
6. Corrosion and valve discoloration observed to date would indicate the necessity of extensive testing before vinyl chloride could be marketed.
7. In view of the above six factors, further work to develop vinyl chloride as an aerosol propellant does not seem justified.

INDEX HEADINGS:

Vinyl chloride, propellant for aerosols
Aerosols - vinyl chloride as a propellant for