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Manual of Hazards to Health From Chemicals Used At The Plants and Laboratories Of Carbide and Carbon Chemicals Corp.

Copy Number

Cooperatively prepared by the
Medical Department, C & C C C
Industrial Toxicology Department, U.C.C.
Works Laboratory, C & C C C, South Charleston
Chemical Hygiene Fellowship, Mellon Institute, Pittsburgh, Pa.

First Edition

May 1, 1949

430

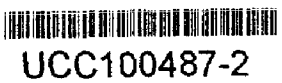
This manual is intended for the use of employees of the Carbide & Carbon Chemicals Corporation who have responsibilities for manufacturing, engineering and research operations. The judgements expressed herein refer to health hazards in chemical manufacturing procedures which are conducted with reasonable care. They stress accidental single exposures as opposed to repeated or substantially continuous exposures. No tabular summary can predict the safety of technical applications of chemicals, particularly where human contact or exposure is inevitable, oft-repeated or prolonged. This manual is not intended for such predictions. Each application must be judged on its own merits, with full knowledge of all the particulars.

The estimates in this manual are based upon experiments with small animals and the experience of industrial physicians. In a large number of instances analogy in chemical structure has been relied upon to allow predictions where no observations have been recorded. The judgements expressed are necessarily tentative and subject to revision as experience accumulates. Despite care used in checking the tables there undoubtedly exist inconsistencies and omissions.

When crude mixtures are being handled the hazards may be somewhat greater than for the partially purified or substantially pure chemicals considered herein.

The undersigned expects to serve as a clearing house for the collection of new observations and corrections in preparation for subsequent editions.

Henry F. Smyth, Jr.
Mellon Institute
Pittsburgh 13, Penna.



GTF Page 4.
5-1-49

Symbols used to describe relative hazard

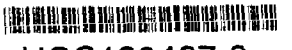
1. No residual injury is to be expected from accidental exposure even if no treatment is applied.
2. Minor residual injury may result from some accidental exposures if no treatment is applied.
3. Major residual injury may result if no treatment is applied.
4. Major residual injury may result in spite of prompt treatment.
5. Physical properties of chemical make the particular exposure almost impossible.

* See supplemental notes on left side of page

* Acetaldehyde
  May sensitize the skin

* Acetoacetacetyl ethylenediamine
  May sensitize the skin

* Acetonylacetone
  Stains the skin brown



Chemical	Relative Hazard of				
	Swallowing	Skin Penetration	Skin Irritation	Breathing Vapor or Dust	Fluid, Dust, or Vapor in Eye
Vanadium (metal)	1	1	1	1	1
"Varsol"	2	1	3	2	3
Victoria blue B base dye	3	3	1*	2	3
Vinyl acetate	2	2	1	3	1
Vinylacetylene	-	-	-	3	1
Vinylbutyl CARBITOL	2	2	1	2	3
Vinyl butyl ether	2	2	1	3	1
Vinyl butyrate	2	2	1	3	1
Vinyl chloride	2	2	2	3	2
Vinyl chloroethyl ether	3	2	1	4	1
2-Vinylcrotonaldehyde	3	4	4*	4	4
Vinyl ethyl ether	2	2	1	3	1
Vinyl 2-ethylhexyl ether	2	2	2	1	2
Vinyl hexyl ether	2	2	2	2	2
Vinyl isobutyl ether	2	2	1	3	1
Vinyl isopropyl ether	2	2	1	3	1
"Vinylite" resins	1	1	1	2	1
"Vinylite" adhesives	1	1	1	2	1
Vinyl 2-methoxyethyl ether	2	2	1	2	3
Vinyl methyl ether	2	2	1	4	1

* See additional notes on left side of this page.

Manufacturing Chemists' A
(FOUNDED 1872)
246 WOODWARD BUILDING — 15TH AND H STS., N. W.
WASHINGTON 5, D. C.
SECRETARY'S OFFICE

October 2, 1953

To Members of: General Safety Committee
Medical Advisory Committee

To Chairmen of: LAPI Committee
Metal Packages Committee
Miscellaneous Packages Committee
Tank Car Committee
Water Pollution Abatement Committee

Subject: Chemical Safety Data Sheet
VINYL CHLORIDE - SD-56

Gentlemen:

Appended hereto is the FINAL draft for the above referred to Chemical Safety Data Sheet. The text contains a number of revisions suggested by members of the Committee and producers and users of vinyl chloride.

In order to comply with our publication schedule it is earnestly requested that all comments and corrections be placed at our disposal not later than October 23.

Copies of the draft are being sent to those producers and users who have received copies of the previous draft in the hope that those paragraphs on which they had commented might be re-examined, and if necessary, deleted or corrected.

The producers and users are The Dow Chemical Company, The Firestone Plastics Company, B. F. Goodrich Chemical Company, Goodyear Tire & Rubber Company, Inc. and Naugatuck Chemical Division, United States Rubber Company.

The writer appreciates very much the cooperation of all concerned in completing the present draft.

Very truly yours,

A. J. Wuertz, Secretary
General Safety Committee

AJW:mbs
Attachment

EX

CHEMICAL SAFETY DATA SHEET SD-56

Properties And Essential Information

For

Safe Handling And Use

Of

VINYL CHLORIDE

Adopted 1953

Chemicals in any form can be safely stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.

SEAL

Manufacturing Chemists' Association, Inc.

246 Woodward Bldg., 15th & H Sts., N. W., Washington 5, D. C.

Chemical Safety Data Sheet

VINYL CHLORIDE

S U M M A R Y

Vinyl chloride is a highly volatile extremely FLAMMABLE compressed gas which is ordinarily handled in liquefied form under pressure. It has a mild anesthetic action in concentrations above 500 ppm. and the vapors are irritating to the eyes.

Precautions necessary in handling the material are detailed in the body of the Safety Data Sheet. Key points to consider for safe handling include:

1. Keep away from heat, sparks and open flame.
2. Provide adequate ventilation.
3. Ground equipment and containers before discharging to reduce danger of ignition from static sparks.
4. In discharging do not heat containers above 50°C. (122°F.). No heat should be applied to tank cars.
5. All equipment etc. should be of steel and have a designed working pressure of at least 100-150 psi.
6. In the event of accidental leaks, spills or whenever excessive vapor concentrations may be encountered only personnel equipped with approved respiratory protection should be permitted in the contaminated area.
7. Chemical safety goggles should be worn when discharging containers or tank cars or whenever there is a danger of the liquid or saturated vapor coming in contact with the eyes.
8. Waste disposal should be away from any source of ignition. Dilute phenolic residues before discharging to sewer.

In case of fire use carbon dioxide or dry chemical extinguishing equipment. In the event of contact with the liquid remove contaminated clothing immediately. For eyes flush immediately with large quantities of water for at least 15 minutes while seeking medical attention.

(WARRANTY CLAUSE)

Mr. Brinton Harmon
The Dow Chemical Company

VINYL CHLORIDE

Adopted October, 1953

1. NAME

Chemical Names:	Vinyl Chloride Chloroethylene Chloroethene
Common Name:	Vinyl Chloride
Formula:	CH_2CHCl

2. PROPERTIES

2.1 Grade

Technical with inhibitor. (Purity of sample 99.42%)

2.2 Important Physical and Chemical Properties:*

Boiling Point	-13.8°C. (+7°F.)
Color	Colorless or water white
Corrosivity	Noncorrosive at normal atmospheric temperatures when dry (moisture free). In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron or steel.
Critical Pressure	52.7 atmospheres
Critical Temperature	158.4°C. (316.8°F.)
Deliquescence	No
Explosive Limits (Percent by Volume in Air)	Lower 4%; Upper 22%
Flash Point	-78°C. (-180.4°F.), Open Cup
Hygroscopicity	No

*Many of the data recorded under this paragraph were determined in the research laboratory of one of the large producers of vinyl chloride and are based on a technical grade material having a purity of 99.42%. Materials from other sources may vary in accordance with the nature of the impurities or the character of the inhibitor present.

Ignition Temperature, Autogenous	472.22°C. (882°F.)
Light Sensitivity	Not a factor in [illegible] chloride
Melting Point . . . . . (Freezing Point)	-153.71°C. (-245°F.)
Molecular Weight	62.50
Odor	Sweet smelling gas.
Physical State	Gas at ordinary temperature and pressure. Liquid under pressure in cylinders or pressure vessels at room temperature.
Reactivity	Polymerizes readily in presence of air, sunlight, oxygen or heat. This behavior is due to the presence of a double bond. Otherwise vinyl chloride is quite stable.
Specific Gravity	.9121 @ 20°/20°C. (water= 1.00)
Vapor Density	2.15 (Air= 1.00)
Vapor Pressure	2580 mm. of mercury 20°C. (68°F.)

2.3 Hazardous Properties

2.3.1 Health Hazards (See 8. Health Hazards and Their Control)

Vinyl chloride presents no very serious problem in general handling aside from the risk of fire and explosion. The presently accepted upper limit of safety as a health hazard is 500 ppm.

2.3.2 Fire Hazard

Vinyl chloride vapors form flammable mixtures with air at all temperatures above -78°C. (-108.4°F.).

3. USUAL SHIPPING CONTAINERS

3.1 Type and Size

3.1.1 Approved ICC cylinders, tank cars and tank trucks designed to carry liquid gases under pressure and provided with safety relief apparatus.

3.1.2 All parts of valve and safety devices in contact with contents of containers must be of metal or other material, suitably treated if necessary, which will not cause formation of any acetylides. A good practice is to dismantle all valves for inspection before each loading. Approved cylinders include ICC - 4B300 and ICC - 4BA300, ICC -

THE DOW CHEMICAL COMPANY
Abbott Road Buildings, Midland

REPORT NO. AA-1001

TECHNICAL SERVICE AND DEVELOPMENT

~~10527~~

Schober, A. E. AA-1001 11-28-58

EVALUATION OF VINYL CHLORIDE AS A PROPELLANT FOR AEROSOL PAINTS

A propellant system comprised of 80% vinyl chloride and 20% propane performs satisfactorily in aerosol paints. Flammability of a paint system containing this system is very similar to current commercial formulations. Polymerization of vinyl chloride did not occur under severe test conditions in the presence of known polymerization catalysts $FeCl_3$, $AlCl_3$ and air.

A savings of 5.4 cents per 16 ounce unit can be realized by aerosol paint fillers if this propellant system is used rather than dichlorodifluoromethane (Freon 12, Genetron 12, Isotron 12). Based on 1957 production figures, 11.9 million pounds of dichlorodifluoromethane were consumed in aerosol paints and thus a 5 to 10 million pound potential exists for vinyl chloride based on 50 to 100% replacement.

Sprays: aerosol, vinyl chloride in paint

(9 220 00 - Halocarbons, Miscellaneous New Applications)

TYPE OF REPORT: Laboratory PAGES: 7

RESEARCH CLASSIFICATION: MATERIAL ____ USE ____ TYPE ____ STAGE ____ DISTRIBUTION ____

DISTRIBUTION: (* COMPLETE REPORT)

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vinyl chloride: as propellant for aerosol paint

INTRODUCTION:

An investigation was conducted to determine which Dow products could be used as low cost propellants for aerosol paints. The aerosol industry currently utilizes dichlorodifluoromethane, (Freon 12, Genetron 12, Isotron 12) hereafter called Propellant 12, as the propellant. Any replacement for Propellant 12 should be a low cost, liquifiable gas, low in toxicity, compatible with paint systems and have a boiling point such that substantial pressure will be exerted by the gas at room temperature. Knowing these requirements it was decided that vinyl chloride should perform satisfactorily as a propellant.

The limitations of vinyl chloride as a propellant were determined. The limitations considered were; vapor pressure, possible polymerization of vinyl chloride containing formulations, flammability of finished formulations and market potential.

The flammability of vinyl chloride would be its primary drawback. However, this should not be a detering factor as present aerosol paints are very flammable.

EXPERIMENTAL WORK:

Vapor Pressure

Propellant 12, the pressurizing agent presently employed, exerts a pressure of 70 psig at 70° F. A typical aerosol paint consists of 60% paint concentrate and 40% Propellant 12. This combination exerts a pressure of about 38 psig at 70° F. Vinyl chloride boils at -13.27° C. and at 70° F. exerts 50 psig. Because paint concentrates are formulated to give a satisfactory spray pattern with Propellant 12 it was, therefore, necessary to increase the pressure of vinyl chloride to give a spray pattern similar to commercial systems. Propane was chosen as it is an inexpensive liquifiable gas exerting a pressure greater than 70 psig at 70° F.

For 70 psig at 70° F., 76.9 vinyl chloride and 23.1% propane were required. This combination when packaged with 60% paint concentrate produced a satisfactory spray. The 60% concentrate and 40%

R&S168023

propellant mix exerted a pressure of 42 psig at 70° F. 42 psig is in excess of allowable package pressure. Commercial systems are packaged in containers in which the pressure may not exceed 40 psig at 70° F. Forty percent of a propellant system (20% propane, 80% vinyl chloride) and 60% paint concentrate exerted an acceptable pressure of 37 psig at 70° F. and produced a satisfactory spray pattern. This 80:20 mixture was used for further evaluation.

POLYMERIZATION OF VINYL CHLORIDE

Because vinyl chloride monomer will undergo polymerization under certain conditions, it was necessary to determine if this could occur in aerosol paint systems. Dow vinyl chloride contains 1000 ppm phenol as a polymerization inhibitor. A literature search revealed that t-butyl catechol is also an effective polymerization inhibitor, while air and certain metals and their salts catalyze polymerization. Tertiary butyl catechol was considered as an alternate inhibitor in the event aerosol packagers considered phenol too toxic.

Aerosols were prepared with two lacquer solvent systems using the vinyl chloride/propane mix as the propellant. System No. 1 is suggested in the CSMA Aerosol Guide while System No. 2 was suggested in the literature.
They are:

	No. 1	No. 2
Methylisobutylketone	75%	-
Butyl acetate	-	75%
Isopropanol	10%	10%
Butyl Cellosolve (Dowanol EB)	10%	10%
Toluene	5%	5%

Aerosol samples were prepared containing variables which could occur in aerosol containers. Our object being to determine if these variables catalyzed polymerization of the phenol containing vinyl chloride and if so, would TBC inhibit the polymerization?

Air, ferric chloride, aluminum chloride and H_2O were chosen as variables being possible in present aerosol systems. Air can be introduced during the filling operation, particularly if the pressure fill technique is employed. Ferric and aluminum chlorides can result if there is any hydrolysis of vinyl chloride and subsequent attack of the steel or aluminum container. Water can be present either as a contaminant during the filling operation or coupled with solvents.

Samples were prepared with the following variables:

1. 100% vinyl chloride/propane + air
2. 100% vinyl chloride/propane + air + 500 ppm TBC*
3. 100% vinyl chloride/propane, no air
4. 100% vinyl chloride/propane, no air + 500 ppm TBC
5. 40% vinyl chloride/propane + 60% No. 1
6. 40% vinyl chloride/propane + 60% No. 1 + 500 ppm TBC
7. 40% vinyl chloride/propane + 60% No. 2
8. 40% vinyl chloride/propane + 60% No. 2 + 500 ppm TBC
9. 40% vinyl chloride/propane + 60% No. 1 + 0.1% anhydrous $FeCl_3$
10. 40% vinyl chloride/propane + 60% No. 1 + 0.1% anhydrous $FeCl_3$ + 500 ppm TBC
11. 40% vinyl chloride/propane + 60% No. 1 + 0.1% anhydrous $AlCl_3$
12. 40% vinyl chloride/propane + 60% No. 1 + 0.1% anhydrous $AlCl_3$ + 500 ppm TBC
13. 40% vinyl chloride/propane + 60% No. 1 + 0.1% distilled water
14. 40% vinyl chloride/propane + 60% No. 1 + 0.1% distilled water + 500 ppm TBC

After two months storage at 120° F., the containers were examined. Samples 1-8 were in excellent condition. No corrosion or polymerization was evident. Samples 9-12 had crystal formations in the liquid phase. The crystals were collected and analyzed. Analysis showed these crystals to be inorganic with no organic material present.

*Tertiary butyl catechol

FLAMMABILITY:

Present aerosol paint formulations containing 60% concentrate and 40% Propellant 12 are very flammable. The completed formulation when sprayed is capable of substaining a flame when the source of ignition is removed. Aerosol paint containing 60% of solvent system No. 1, 32% vinyl chloride and 8% propane were prepared and subjected to the same flame test. No appreciable difference was noted between this formulation and the above mentioned commercial formulation as far as flammability was concerned. The flame of the vinyl chloride-propane containing system was blue while the other system was a typical yellow.

MARKET POTENTIAL:

Vinyl chloride was considered primarily a propellant for aerosol paints. However, it should be applicable in any aerosol formulation where flammability is not a drawback. This would include presently flammable formulations and formulations used only outdoors such as weed killers and outdoor insecticides.

In 1957, 36.5 million cans of aerosol paints were produced*. To fill these cans 29.7 million pounds of complete formulations was required. Most formulations consisted of 60% concentrate and 40% Propellant 12. Based on this ratio, 11.9 million pounds of Propellant 12 were consumed. At present it is difficult to determine the sales volume of aerosol weed killers and outdoor insecticides.

Propellant 12 is 26.3 cents per pound in tank cars. The use of the vinyl chloride/propane propellant system would result in a savings of 5.4 cents per 16 ounce container, assuming the propellant to constitute 40% of the weight. This savings would be the primary reason for any manufacturer using vinyl chloride/propane rather than Propellant 12.

At present vinyl chloride is being used as a propellant in Japan and Germany. The reason expressed for its lack of usage in the United States at present is its flammability and the subsequent

*AA Report 907

dangers encountered in filling. However, current aerosol paints are flammable and many manufacturers have installed explosion proof equipment to avoid such accidents as happened to Thomasson of Pennsylvania (Krylon) several years ago when the paint concentrate caught fire destroying the entire operation. Therefore, the use of vinyl chloride/propane should not entail expensive modification of existing filling equipment.

CONCLUSIONS:

1. Eighty percent vinyl chloride and 20% propane can be used as a replacement for Propellant 12 in aerosol paints resulting in a savings of 5.4 cents per 16 ounce can.
2. Under most conditions encountered in aerosols, polymerization of vinyl chloride would not occur.
3. Flammability of aerosol paints containing vinyl chlorides/ propane is not noticeably greater than commercial systems.
4. In most aerosol plants filling equipment would not have to be altered to use vinyl chloride/propane.
5. If vinyl chloride/propane were used exclusively in 1957, 9.5 million pounds of vinyl chloride would have been required.

The following companies are engaged in production of aerosol paints:

Acrolite Products, Incorporated
106 Ashland Avenue
West Orange, New Jersey

Capital Packaging
1441 South Circle Avenue
Forest Park, Illinois

T. J. Dunham Paint Company
115 Woodward Avenue
Yonkers, New York

Inland Paint and Chemical Company
2144 West 49th Street
Chicago, Illinois

Kerr Chemical Company
9 South Farview Avenue
Park Ridge, Illinois

Red Ram Chemical Company
755 Utica Avenue
Brooklyn 3, New York

Red Devil Chemicals, Incorporated
30 North West Street
Mount Vernon, New York

Red Lion Chemical Co.
146 North Charles Street
Red Lion, Pennsylvania

Ronor Corporation
1360 West Ninth Street
Cleveland, Ohio

SprayOn Products Company
2075 East 65th Street
Cleveland, Ohio

Stalfort Pressure-Pak
321 West Pratt Street
Baltimore 1, Maryland

Thomasson of Pennsylvania, (Krylon)
Norristown, Pennsylvania

Cleveland Aerosol Packaging
9801 Harvard Avenue
Cleveland 5, Ohio

caj

Mr. P. G. Magnusson

May 27, 1959

292 Madison Avenue - 4th Floor

TECHNICAL SERVICE

Mr. R. A. Corio
Dr. C. U. Dernehl

Dear Mr. Magnusson:

We are attaching a copy of a letter from The Pentasote Company concerning a toxicity problem that they encountered in the use of vinyl chloride. They have previously spoken with Dr. Dernehl on the telephone about this problem, and the letter is as a result of our request that they advise us in writing of just what type of information they would like us to send them.

Dr. Dernehl has advised that working up the information on case histories would be rather time consuming and require a considerable amount of work on someone's part. We need to decide how much information and how much time we wish to spend in supplying this information to this customer. We would appreciate your discussing it with Dr. Dernehl and advising him how far he should go in getting together information that would be helpful to The Pentasote Company.

Very truly yours,

ORIGINAL SIGNED BY
C. P. MC CLELLAND

CPMcClelland/nf
Attachment

10 0928 Vinyl Chloride: as propellant for aerosols

THE DOW CHEMICAL COMPANY
Midland, Michigan

PROBLEM NO. 9 218 00

09261

TECHNICAL SERVICE AND DEVELOPMENT

REPORT NO. AA-1154

Kaufman, J. D. J. D. Kaufman AA-1154 7-29-59

EVALUATION OF VINYL CHLORIDE AS A PROPELLANT FOR AEROSOLS

Experimental work has been conducted on mixtures of vinyl chloride with chlorofluorocarbon aerosol propellants to determine flash point characteristics and explosive limits. This work has shown that a mixture of 25% vinyl chloride, 37 1/2% Propellant 11 and 37 1/2% Propellant 12 could replace a 50-50 mix of propellants 11 and 12 without increased hazard during filling operations or excessive flammability of the final product. This 50-50 mix of 11 and 12 is representative of the propellant component of many commercial aerosols. Further, the work has shown that a mixture of 16% vinyl chloride, 4% Propane and 80% Propellant 12 could similarly replace the pure Propellant 12 now used for pressurizing aerosol paints. These aerosols would represent a potential total market for 30,000,000 pounds of vinyl chloride based on present aerosol sales. Since vinyl chloride does not have strong odor or strong solvency properties and is more easily evaporated than methylene chloride or Chlorothene, it would not meet the sales resistance on these points that those two products have. The patent picture is encouraging. Since customers have some reservations about handling highly flammable propellants, it will probably make necessary the sale by Dow of blended mixtures. Although more work on this project seems desirable, the influence of current sales policy and profit considerations must be weighed before proceeding.

(9 218 00 Halocarbons In Aerosols, General)

TYPE OF REPORT: Laboratory and Market Research Report PAGES: 13

RESEARCH CLASSIFICATION: MATERIAL — USE — TYPE — STAGE — DISTRIBUTION

DISTRIBUTION: (* COMPLETE REPORT)

Vinyl Chloride: mixtures with dichlorodifluoromethane and trichlorofluoromethane, flash points and explosive limits

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R&S168008-1

Page 001

R&S168008

INTRODUCTION

In AA Report 1001, A. E. Schober discussed the potential for vinyl chloride in aerosols. Laboratory work indicated that Propellant D (80% vinyl chloride, 20% propane) would serve as a complete replacement for Propellant 12 (dichlorodifluoromethane) in aerosol paints. This investigation covered vapor pressure characteristics, polymerization difficulties, and flammability problems. Paints seemed to be the major market for a vinyl chloride based propellant since many flammable solvents are used in a paint concentrate and the finished product is very flammable. It was felt that the potential for vinyl chloride in other areas would be restricted due to the necessity for precautionary labeling on cans and modification of filling lines to handle more dangerous materials.

A study of markets for propellants in that report indicated a 5 to 10 million pound potential for vinyl chloride if Propellant D was employed as a total replacement for Propellant 12 in paint aerosols. Price authorization was obtained (0.12 per pound F.O.B. Freeport in 4000 gallon cars) and extensive field contacts were made to determine customer interest. Questions raised by customers indicated that further information about the material would be necessary, but that the cost saving appeared quite appealing.

Customer contact indicated that while flammability considerations relating to labeling were important, the requirements of the ICC in relation to shipping flammable aerosols were more important. These ICC requirements demand that the flash point of the contents of a standard aerosol container be above 20°F. This is not difficult to achieve when a fluorochlorocarbon is used as a propellant but limits the applicability of vinyl chloride severly since the pure material has a flash point of -108°F.

Paints use pure Propellant 12 as a pressurizing agent since the paint concentrate depresses the pressure of 12 to less than 40 pounds at 70°F., in the finished product - a requirement for beer can type aerosols. Other aerosols use mixtures of Propellant 11 (trichlorofluoromethane) and Propellant 12 to attain a pressure of 38 pounds at 70°F. Pure vinyl chloride by itself exerts a pressure of 38 pounds at 70°F. The propane is added to Propellant D to raise the pressure of the mixture to that of Propellant 12.

Various customers pointed out that mixtures of vinyl chloride with Propellants 11 and 12 might produce a finished aerosol which would pass the ICC test. Further, a mixture which had no explosive limits could probably be used safely in all present filling equipment without modification. Although the ICC regulations seemed to sharply reduce the potential for vinyl chloride in paint aerosols, the other possiblity and customer interest opened up broad new markets for vinyl chloride. Further laboratory work was in order to determine the flammability and explosive characteristics of mixtures of vinyl chloride, Propellant 11 and Propellant 12.

EXPERIMENTAL

The laboratory work covered in this report breaks down quite naturally into two areas, the investigation of flash points of finished aerosols containing flammable propellants and the explosive hazards of mixtures of vinyl chloride with the fluorinated propellants.

A. FLASH POINT DETERMINATIONS ON PROPELLANT D MIXTURES

Some years ago, the ICC regulations required the use of a special container for aerosols classified as flammable. Due to the higher cost of this container, a special exemption was granted allowing the shipping of a flammable product in

a regular container, provided the contents flashed above 20°F. This requirement seems to cause little difficulty at present as shown by tests 1-4:

TABLE I

Sample No.	Propellant	Concentrate	Flash Point
1	100%-12	Formula III*	119°F.
2	100%-D	Formula III	<-25°F.
3	100%-12	Comml. conc. No. 1**	96°F.
4	100%-12	Comml. conc. No. 2**	86°F.
5	30%-D 70%-12	Comml. conc. No. 1	38°F.
6	30%-D 70%-12	Comml. conc. No. 2	38°F.
7	30%-D 70%-12	Formula III	38°F.
8	30%-D 70%	Formula III With 50% of MIBK replaced with methylene chloride	38°F.
9	10%-BCDF 30%-D 60%-12	Formula III	62°F.
10	10%-BCDF 40%-D 50%-12	Formula III	<-22°F.

* From Pressurized Packaging by Herzka and Pickthall. It contains 24.4% solids (nitrocellulose 43.5%, non oxidizing alkyd 43.5%, dibutyl phthalate 13.0%) and 75.6% solvents (Methylisobutyl ketone 80%, Dowanol EB 10%, isopropanol 5%, Ethanol 5%) and is mixed 50% by weight concentrate, 50% Propellant 12.

** Obtained from aerosol fillers

Three samples were prepared using Propellant 12 as the sole pressurizing agent. When Propellant D replaced the Propellant 12 entirely, flash points well below 0°F. were obtained.

Extensive testing showed a straight line relationship between % of Propellant D in the pressurizing portion and the flash point of the finished product when the %

of Propellant D in the total propellant mix did not exceed 35%. (See Figure I) When the ratio of D to 12 was 35/65, the flash point of finished paint was approximately 20°F. Increasing the ratio of Propellant D above this value seemed to result in a sharp decline in flash point to well below 0°F. It appears that if the percentage of D is below 35, the propane flammability is suppressed by the Propellant 12. Concentrations of D over 35%, result in a concentration of propane over 7% in the total propellant mix. Since propane is the most volatile flammable component, it would be expected to give very low flash points when present even in low concentrations.

A ratio of 30% Propellant D, 70% Propellant 12 was chosen to give a margin of safety and this propellant mix tested with several aerosol paint concentrates and all flashed at 38°F. Concentrates 1, 2 and 3 above, were tested as well as another commercial concentrate. Even when 1/2 of the methyl isobutyl ketone in concentrate No. 1 was replaced with methylene chloride, the end product flashed at 38°F. (See Table I, tests 5-8).

Various mixtures of bromochlorodifluoromethane with Propellant 12 and Propellant D were tested. A mixture of 10% bromochlorodifluoromethane, 30% Propellant D, 60% Propellant 12, was used as pressurizing agent with concentrate No. 1 and the product flashed at 61°F., but when a mixture of 10% bromochlorodifluoromethane, 40% Propellant D, 50% Propellant 12 was mixed with concentrate, it flashed at -22°F. This would tend to show that bromochlorodifluoromethane would be of limited value in raising the flash point of aerosol paints, since it is quite a bit more expensive than Propellant 12 or Propellant D. (See Table I, tests 9-10).

B. FLASH POINT DETERMINATIONS ON VINYL CHLORIDE MIXTURES

To determine the applicability of vinyl chloride in non-paint aerosols, a series of experiments using vinyl chloride itself rather than Propellant D were carried out. Various mixtures of Propellant 12 with vinyl chloride and one of the three commonly used vapor pressure depressants were prepared. These were tested by themselves without any concentrate for flash point. A mixture of 36.4% Propellant 11, 36.4% Propellant 12, 27.2% vinyl chloride, gave no flash to dryness. This mixture possibly could be used as a replacement for 50% Propellant 11, 50% Propellant 12 mixtures now sold for such products as space deodorants, hair sprays, insecticides, etc., if other factors were all right.

This mixture was tested for pressure with a pressure cylinder and gauge arrangement used in earlier pressure determinations in Technical Service and Development. Theoretical calculations show that any mixture of 50% Propellant 11, 50% Propellant 12, with vinyl should have a pressure of 38 psig at 72°F., if they form an ideal solution. The actual readings taken were 5 pounds higher at 70°F., which would exceed the pressures allowed in beer can type aerosols. Lower pressures could be easily obtained by reducing the ratio of Propellant 12 to Propellant 11 which would also reduce costs since Propellant 12 costs roughly $0.05 per pound more than Propellant 11.

Mixtures of Propellant 12, vinyl chloride and methylene chloride or Propellant 12, vinyl chloride and Chlorothene were tested but these latter two compounds seemed less effective than Propellant 11 in suppressing flash points.

C. EXPLOSIVE LIMIT DETERMINATIONS

From the safe handling standpoing, a propellant which

presents no explosion hazards is desired by aerosol fillers. Equipment was available in the gas laboratory for running explosive limits of various materials. The equipment differed in several details from that used by the Bureau of Mines for similar tests. Although these differences may have some effect on the data derived, it is felt that the information obtained is reasonably close to that which would have been obtained with the other equipment. However, some anomalous results were recorded with the gas laboratory equipment and it is felt that any further work should be done with apparatus which is similar in all respects to the Bureau of Mines apparatus.

The literature indicates that propane forms explosive mixtures with air when propane is present in quantities from 2% to 9%. Vinyl chloride has limits of 4% to 22%. The gas laboratory reported that Propellant D had limits of 4% to 15%. Following work on flash points, a mixture was prepared in an aerosol can which consisted of 70% Propellant 12, 30% Propellant D. When this liquid was vaporized and tested, it exploded in the range of 9.5% to 23.5% of the mixture in air. Various ratios of Propellant D to Propellant 12 were formulated and tested.

% Propellant D	% Propellant 12	Lower Limit	Upper Limit
30	70	9.5	23.5
25	65	13.0	Not tested for
20	80	17.0	19.5
18	82	No explosive mixtures found	

Mixtures of 50% Propellant 11, 50% Propellant 12, with varying quantities of vinyl chloride were prepared and tested.

% Vinyl Chloride	%50-50 Mixture	Lower Limit	Upper Limit
27.2	72.8	18	26.5
26.4	73.6	19.5	24.5
26.0	74.0	No explosive mixtures found	

CONCLUSIONS FROM LABORATORY WORK

1. Mixtures of Propellant D with Propellant 12 can not exceed 35% Propellant D if the final aerosol paint is to pass the ICC test for flammability. A 30-70 mix gives a desired margin of safety.

2. Bromochlorodifluoromethane does not effect flammability sufficiently but may have more influence on explosive limits.

3. A mixture of 27.2% vinyl chloride, 36.4% Propellant 12 and 36.4% Propellant 11 with no concentrate had no flash point to dryness. Since most concentrates are non-flammable, finished aerosols using this mixture for pressurizing should pass the 20°F. flash test easily.

4. Mixtures of less than 26% vinyl chloride in a 50-50 mix of 11 and 12 had no explosive limits.

5. Mixtures of less than 20% Propellant D with 80% Propellant 12 had no explosive limits.

AREAS FOR FUTURE LABORATORY WORK

1. Determine the explosive limits with equipment constructed in accordance with the Bureau of Mines suggestions.

2. Determine the effect of bromochlorodifluoromethane and related materials on explosive limits. Although bromochlorodifluoromethane did not appreciably change flash point characteristics, it might have greater effect on explosive

limits at economically feasible concentrations.

3. Explore the effect of vinyl chloride in various formulations. Although it has low odor, evaporates readily and has only moderate solvency (these have been objections to both methylene chloride and Chlorothene) there may be other factors which need to be considered.

4. Explore possibility of obtaining patents on various mixtures for use in aerosols. A Canadian patent (No. 541,786) has been issued for a mixture of Propellant 11, Propellant 12, and isobutane and an American patent is understood to be applied for.

5. Explore the possibility of modifying ICC regulations concerning shipping aerosols. The 20°F., flash point seems very arbitrary and it is conceivable that another test could be devised which would be a better indication of safety but would allow the inclusion of more vinyl chloride.

6. Investigate further the flash point and explosive characteristics of mixtures of Chlorothene, vinyl chloride and Propellant 12, as well as mixtures of methylene chloride, vinyl chloride and Propellant 12. Though these two Dow products are less effective than Propellant 11, supressing flash points, they may be worth considering since they sell for less than Propellant 11.

DISCUSSION

These areas of investigation are interesting but it was decided that sufficient data was now available to determine the market potential for vinyl chloride in aerosols to enable a decision concerning continued activity in this area.

The potential markets can be broken down as follows:

Product	Cans Filled In 1958 ($X10^6$)	Estimated Average Can Size	Estimated % Propellant In Can	Cost Saving To Filler Per 10,000 Cans*	Estimated Propellant Consumed Lbs. ($X10^6$)
Hair Sprays	120	1/2 lb.	70	$ 78.00	42
Space Insecticides	30	3/4 lb.	90	$150.00	20
Room Deodorants	60	1/2 lb.	95	$106.00	30
Residual Insecticides	24	3/4 lb.	80	$133.00	15
Paints	40	1 lb.	45	$108.00	18

* Based on a delivered price of vinyl chloride or Propellant D of $0.14 per pound. These figures are very close to those obtained when a filler uses Chlorothene or methylene chloride as a 50% replacement for Propellant 11.

The first four categories represent a market for vinyl chloride alone, since they predominantly use mixtures of Propellant 11 and Propellant 12. Paints would utilize Propellant D, since they currently use Propellant 12 exclusively. Since experimental work indicates a maximum of 20% Propellant D, 80% Propellant 12 or 25% vinyl chloride, 75% Propellant 11-mix form non-explosive mixtures, the total potential market in these products is as follows:

Product	Lbs. Total Propellant	Lbs. Propellant D	Vinyl Chloride
Paints	18,000,000	3,600,000	2,800,000
Hair Sprays	42,000,000	-----	10,500,000
Space Insecticides	20,000,000	-----	5,000,000
Room Deodorants	30,000,000	-----	7,500,000
Residual Insecticides	15,000,000	-----	3,750,000
			29,550,000

Since the propane raw material cost is very low, we may consider Propellant D as little different from pure vinyl chloride. Thus, the total potential market for vinyl chloride in these aerosol products is 30,000,000 lbs. It would seem reasonable to expect Dow to capture 33% of this market or 10,000,000 lbs.

These five product areas represent 280,000,000 cans. 100,000,000 cans of products such as shaving lather and dental cream were produced last year, but represent little potential for vinyl chloride. Smaller miscellaneous uses add up to another 90,000,000 cans which might represent some market for vinyl chloride but are difficult to evaluate at present.

The aerosol market has grown at 20% per year in the past and is still growing quite rapidly. The potential for vinyl chloride would expand along with this growth.

FACTORS INFLUENCING A DECISION CONCERNING FURTHER WORK

1. Advantages

   A. Laboratory and market data indicate a reasonable Dow market for vinyl chloride in aerosols of 10,000,000 lbs. In proportions indicated above, it would present no fire hazard, and would not seem to cause difficulty from odor, wet spray or high solvency as do methylene chloride and Chlorothene. The cost saving to the aerosol filler for mixtures of vinyl chloride or Propellant D would be about the same as those obtained with methylene chloride or Chlorothene. The product would therefore seem to present few sales hurdles.

   B. Good possibility exists for patenting a mixture of vinyl chloride with some of the fluorinated propellants. This patent could be licensed even if no effort was made by Dow to sell vinyl chloride. Maximum sales of vinyl chloride would require active promotion by Dow.

   C. If Dow chose to market a Propellant 11-12 vinyl chloride mixture, a discount on purchases by Dow of the Propellant 11-12 mix would appear reasonable, since Dow would be providing the sales and technical service effort.

D. It would establish Dow as a propellant supplier and would thereby aid sales of methylene chloride, and Chlorothene.

E. The sale of 10 million pounds of vinyl chloride for blending would entail the purchase of about 30 million pounds of fluorinated materials. This would establish Dow as the major consumer of these chemicals. Such a status would likely strengthen our sales position as a supplier of carbon tetrachloride and chloroform to the propellant producers.

F. It is possible that small quantities of brominated hydrocarbons would favorably influence the explosive characteristics of vinyl mixtures. This might mean greater percentages of vinyl as well as the inclusion of other Dow products.

2. Disadvantages

A. It would be necessary to handle at terminal points and sell, approximately three pounds of fluorniated propellants for each pound of vinyl chloride unless the customers bought the vinyl chloride directly and did their own mixing. It is not know at present how many customers would be willing or able to do this.

B. Heavier technical service would be requested. It is estimated that 5-10 people would be necessary to develop and promote the material.

C. The product would compete in some areas with Chlorothene and methylene chloride and could reduce the sales of these products.

D. The accepted M.A.C. for vinyl chloride is 500 ppm which should not represent a serious hazard. However, our

Biochemistry Laboratory indicates that it may request a lowering of this M.A.C. by the Conference of Governmental Industrial Hygienists as a result of experimental work now in progress.

CONCLUSIONS

1. From a technical and market standpoint, a sizeable potential exists for vinyl chloride. Before conducting further work in this area, guidance by management based on sales policy and profitability is required.

INDEX HEADINGS

Vinyl Chloride, Propellant For Aerosols

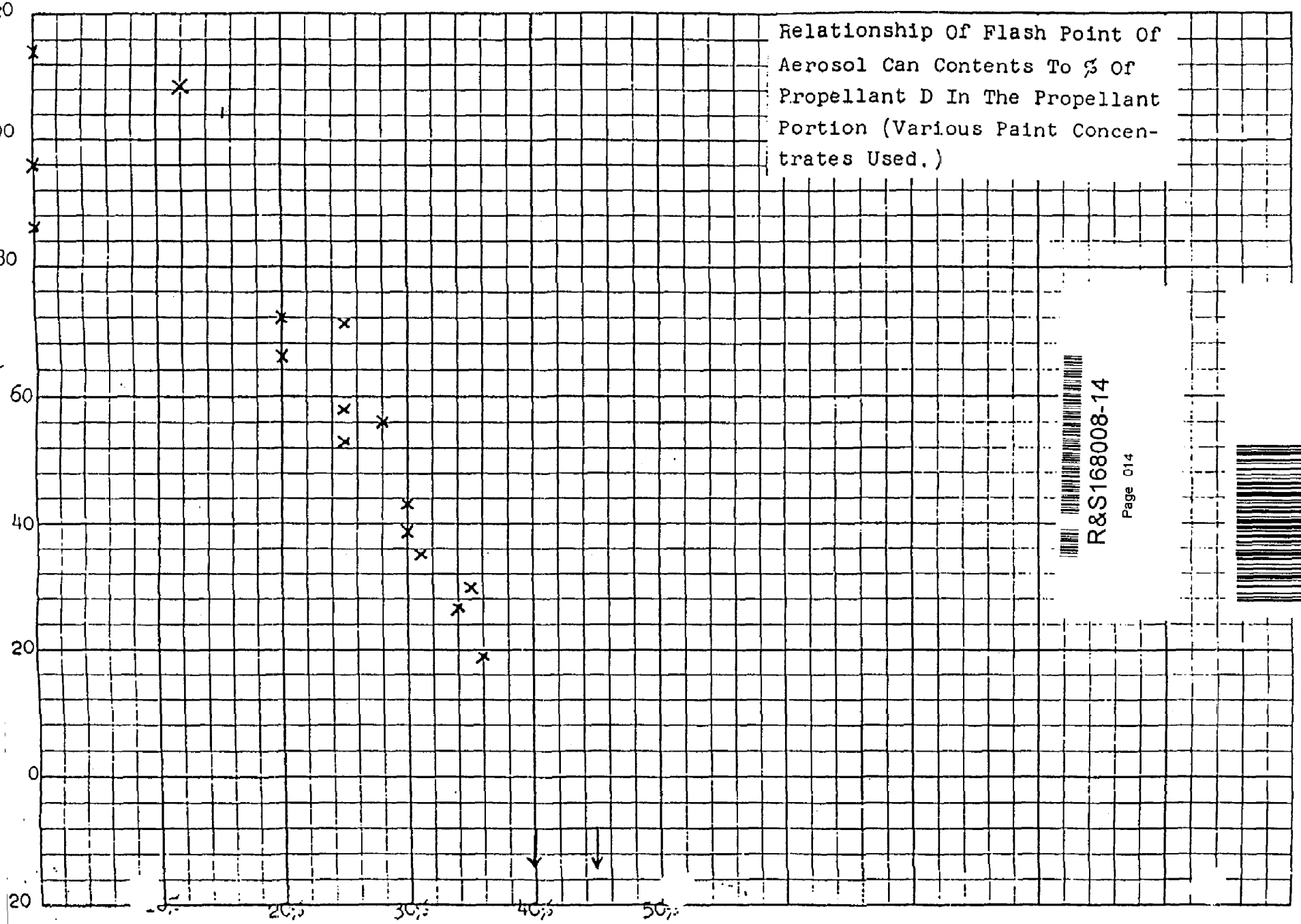
Flash Point, Mixtures of Vinyl Chloride With Dichlorodifluoromethane and Trichlorofluoromethane

Explosive Limits, Mixtures of Vinyl Chloride With Dichlorodifluoromethane and Trichlorofluoromethane

Flash Point, Mixtures of Propellant D With Dichlorodifluoromethane and Trichlorofluoromethane.

Bromochlorordifluoromethane, Flash Point Supression of Propellant D and Dichlorodifuloromethane.

FIGURE I



02724

AN2287

Excerpt from letter written by Dr. E. Mastromatteo, Division of Industrial Hygiene, Department of Health Province of Ontario, dated October 13, 1959, re Vinyl Chloride experiments on small animals.

On April 14, 1959, groups of 5 animals comprising 5 mice, 5 rats and 5 guinea pigs were exposed to varying concentrations of vinyl chloride in air for a period of 30 minutes. The exposures were conducted in a special animal chamber. Concentrations of 10, 20 and 30 per cent of vinyl chloride in air were used. An addendum to this letter will describe how these concentrations were calculated. An additional group of 5 guinea pigs was exposed to a concentration of 40% vinyl chloride in air on the same date. In all, 65 experimental animals were involved, including 15 control animals. The control animals comprised 5 mice, 5 rats and 5 guinea pigs, and these control animals came from the same animal stocks and were fed and housed in the same manner as the other animals.

A summary of the results obtained is given below:

Ten Per Cent Vinyl Chloride in Air

Mice	All were lying down at the end of 30 minutes showing tremors and twitching; recovery was quick in fresh air; no deaths.
Rats	All were lying still at the end of the experiment; recovery was quick in fresh air; no deaths.
Guinea Pigs	One was in side position; four were standing; recovery was quick; no deaths.

Twenty Per Cent Vinyl Chloride in Air

Mice	One mouse was dead; four were unconscious; recovery in fresh air took about ten minutes.
Rats	All unconscious with shallow, rapid respirations; recovery took about ten minutes in fresh air; no deaths.
Guinea Pigs	All were in side position; recovery in fresh air took about 20 minutes; no deaths.

Thirty Per Cent Vinyl Chloride in Air

Mice	All five mice dead.
Rats	All five rats dead.
Guinea Pigs	All five were alive but unconscious with shallow rapid respiration. One guinea pig from this group died after 24 hours.

Forty Per Cent Vinyl Chloride in Air

Guinea Pigs	Only guinea pigs were exposed. One was dead and four were unconscious at the end of the experiment. Another one died within 24 hours after exposure. Recovery after exposure to fresh air in those which survived was slow.

20532001

Excerpt continued..........

Post Mortem Examination

All animals which died as a result of exposure to vinyl chloride on April 14th, 1959, were dissected within two hours. I carried out these dissections and I made observations on the gross changes present. Various tissues were removed and preserved in five per cent formalin for later detailed microscopic study.

The two guinea pigs showing delayed death were likewise dissected the following day.

All exposed animals which survived were killed on April 27, 1959 (13 days after they were exposed to vinyl chloride). I performed dissections on all of these and tissue specimens were also taken and preserved in five per cent formalin.

Control animals from the same animal stocks and housed under similar laboratory conditions were killed in the same manner and post mortem examinations conducted in the same way. There was, of course, no exposure to vinyl chloride with this group.

In general, all animals which died as a result of exposure to vinyl chloride showed congestion and/or haemorrhage of the lungs and congestion of the liver and spleen. The control animals did not show these changes.

I transported the tissues preserved in formalin to Dr. H. Danziger of Welland. Dr. Danziger had agreed to prepare these sections for microscopic study, and to examine them.

Yours very truly,

(Signed)

E. Mastromatteo, M.D.,
Division of Industrial Hygiene

APPENDIX

Concentrations of vinyl chloride gas mixed with air, ranging from 5% to 40% vinyl chloride, were delivered to a 56-liter capacity animal test chamber.

Vinyl chloride gas and air were delivered through a rubber tube to the animal chamber. This tube had a glass Y with connections to 1) a "Fisher" flow meter and the vinyl chloride supply tank, and 2) a "Precision" wet-test gas meter and standard air pump. The flow rate of vinyl chloride was adjusted by means of a valve on the supply tank and of the air by adjusting the pump rate.

Fresh air and vinyl chloride in the desired proportions were obtained by the flow pool through the Y tube and rubber tube from the measured and controlled sources. The combined rate of flow for the 5% to 20% concentrations was 12 liters per min. and for the 30 and 40% concentrations the rate was 8 and 6 liters per minute respectively.

INTER-COMPANY CORRESPONDENCE

(INSERT NAME) COMPANY U.C.C. LOCATION Mellon Institute

TO Dr. T. W. Hale
LOCATION New York Office

ATTENTION
COPY TO Dr. E. R. Weidlein, Jr.
Dr. A. W. Downes

DATE November 24, 1959
ANSWERING LETTER DATE
SUBJECT

Dear Tom:

You will recall that the current threshold limit for vinyl chloride is 500 p.p.m., based largely on single guinea pig inhalation studies by the Bureau of Mines about 25 years ago.

An off-the-record phone call from V. K. Rowe gives me incomplete data on their current repeated inhalation study. Six months at 500, 200 and 100 p.p.m. has not found a no-effect level. Even 100 p.p.m. produced organ weight changes and gross pathology, with micropathology expected. Vinyl chloride monomer is more toxic than has been believed. Rowe expects to get more information before he decides whether or not this has any bearing on the safety of packaging uses of vinyl resins.

Dow has been disturbed at sales efforts saying chloroform is less toxic than carbon tet. They have completed six months inhalation and find chloroform like carbon tet. This means its threshold limit will be lowered, as I have suggested for years. It was originally set by analogy with carbon tet, and never lowered when that for carbon tet was reduced.

I suggest that these personal communications not be quoted until Dow publishes.

Very truly yours,

Henry F. Smyth, Jr.

and

RECEIVED
NOV 27 1959

THIS FORM FOR INTER-COMPANY CORRESPONDENCE ONLY

011-1959-00003891

Vinyl Chloride
Digital Process Inventions, Litigation Support
(304) 522-1810

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THE DOW CHEMICAL COMPANY

Midland

PROBLEM NO. 9 218 00

13548

TECHNICAL SERVICE AND DEVELOPMENT

Kaufman, J. D. OK AA-1216 11-30-59

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

REPORT NO. AA-1216

TYPE OF REPORT: Final PAGES: 9

RESEARCH CLASSIFICATION: MATERIAL ____ USE ____ TYPE ____ STAGE ____ DISTRIBUTION ____

DISTRIBUTION: (* COMPLETE REPORT)

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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.

WOB 3172

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.

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.

WOB 3174

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.

WOB 3175

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

WOB 3176

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

THE DOW CHEMICAL COMPANY

Midland

PROBLEM NO. 9 218 00

TECHNICAL SERVICE AND DEVELOPMENT

13548

REPORT NO. AA-1216

Kaufman, J. D. OC AA-1216 11-30-59

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

TYPE OF REPORT: Final PAGES: 9

RESEARCH CLASSIFICATION: MATERIAL ____ USE ____ TYPE ____ STAGE ____ DISTRIBUTION ____

DISTRIBUTION: (* COMPLETE REPORT)

* MIDLAND CRI (3 Copies)

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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.

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

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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