10 0928 Vinyl Chloride: as propellant for aerosols

THE DOW CHEMICAL COMPANY
Midland, Michigan

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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.

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

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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

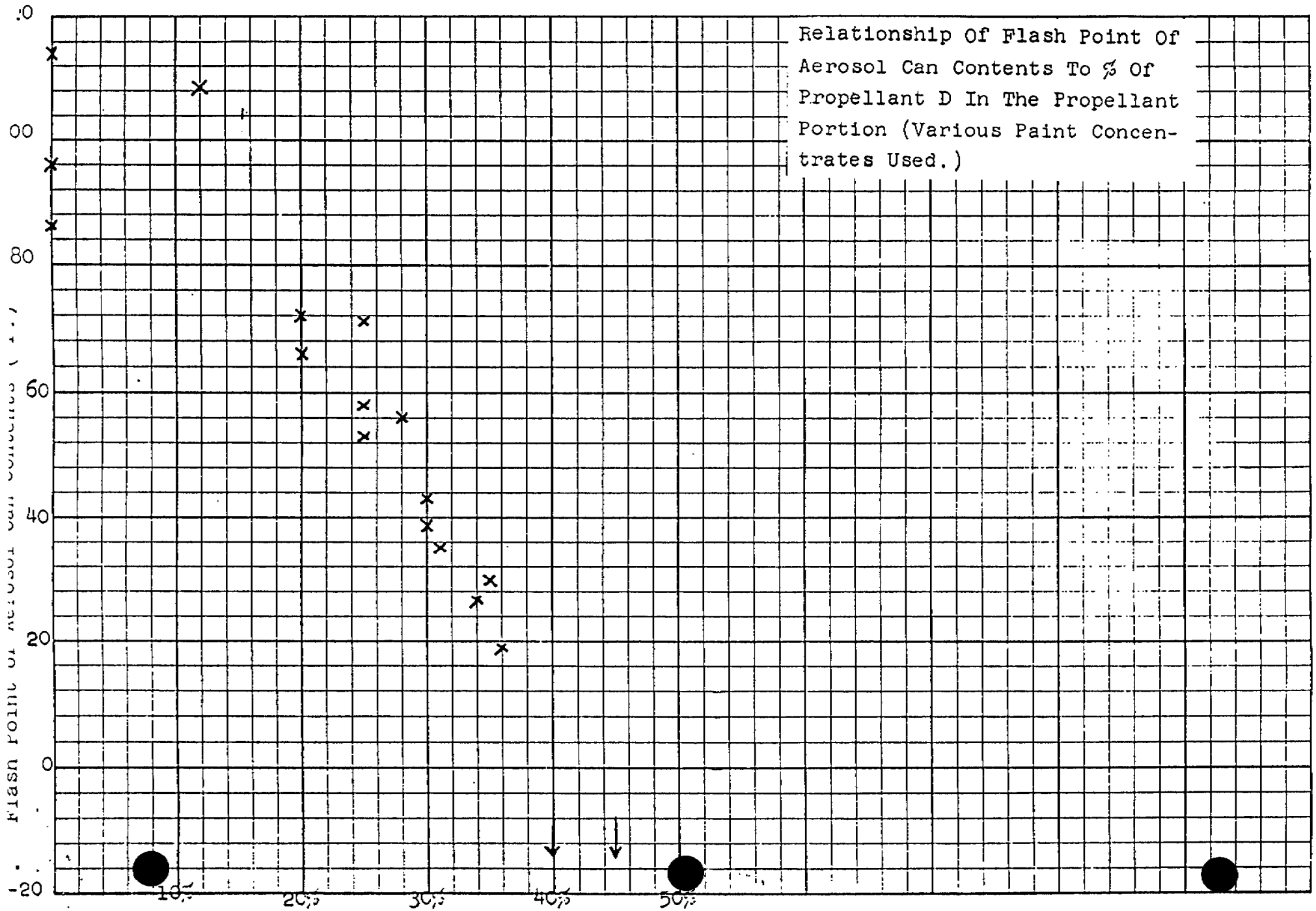
Flash Point, Mixtures of Vinyl Chloride With Dichlorodifluoromethane and Trichlorofluoromethane

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


Relationship Of Flash Point Of Aerosol Can Contents To % Of Propellant D In The Propellant Portion (Various Paint Concentrates Used.)
Flash Point Of Aerosol Can Contents (°F.)
100
80
60
40
20
0
-20
10%
20%
30%
40%
50%