10 0780

THE DOW CHEMICAL COMPANY
Abbott Road Buildings, Midland

REPORT NO. AA-1001

TECHNICAL SERVICE AND DEVELOPMENT

Schober, A. E. A E Schober AA-1001 11-28-58 10527

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

RECEIVED
OCT 16 1959
CENTRAL RESEARCH INDEX
INDEXED
S.W.E. SEP 24 '59

(9 220 00 - Halocarbons, Miscellaneous New Applications)

TYPE OF REPORT: Laboratory PAGES: 7

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

DISTRIBUTION: (* COMPLETE REPORT)

COPIED IN MIDLAND CRI
MAY 25 1999

* MIDLAND CRI (3 Copies)
• EXECUTIVE RESEARCH

*J. C. Van Horn
*A. J. Pastor
*E. W. Larabee, ARB
*W. U. Seiler, ARB
*R. L. Brown, 433
*R. K. Treichler, Fpt., A-2421
E. B. Barnes, Fot., B-1210
*A. E. Schober
*W. C. Bauman, 687
*Problem No. 9 220 00
TS&D Files
*J. D. Kerr
*D. K. Ballman, 47
*T. J. Christiansen, ARB
*N. R. Peterson, 433
W. A. Henson. 433
R. H. Smith, Fpt., B-121
*M. E. Pruitt, Fpt., B-1215
*M. J. Stoesser, Sarnia
R. A. Lindsay
O. C. Cessna

vinyl chloride: as propellant for aerosol paint

R&SI68022

FOR USE OF DOW EMPLOYEES ONLY

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&SI68023

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?

R&S168024

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

R&S168025

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

R&S 68026

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

R&S168027

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

R&S168028