Mr. A. B. Chivvis
UCC Olefins Division
28th floor - N. Y.

January 16, 1967

Mr. J. M. Bilderback

Aerosol Booklet

Dear Mr. Chivvis;

Enclosed is a revision of the aerosol booklet that was put together about a year ago. The Appendix, which made up nearly half of the previous work, has been removed; the introduction has been redone and some Silicones formulations have been added. Assorted other corrections and changes have been made throughout the text.

On Page 11 mention is made of methylene iodide as an inhibitor. The purpose here is to provide public disclosure of methylene iodide as an inhibitor so as to preclude anyone else patenting it.

It would be appreciated if you would review the booklet and, if you think it could be used to advantage, please send it on to Mr. Bilderback for his review and comments also.

Very truly yours,

RJ Scott/cao
Enclosure

AEROSOL

HANDBOOK

(Hex) UCON Aerosol Chemicals

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IMPORTANT

Union Carbide is a supplier of a complete line of propellants and chemicals to the aerosol industry. Fluorocarbons, hydrocarbons, vinyl chloride, dimethyl ether, specialty blends, compressed gases, alcohol, solvents, and other materials are available from this single source. Their use varies widely over a range of nineteen categories of aerosol products, as differentiated by the CSMA. Which propellant, solvent or other component is to be used in a given instance depends upon the product itself. This book does not cover the technology of all of the products involved in the nineteen categories, but basic technology is presented which can be helpful in solving formulation and product development problems. In addition, the resources of Union Carbide are available to you for further assistance.

I. INTRODUCTION

A. What Is an Aerosol?

Scientifically, an aerosol is a suspension of fine solid or liquid particles in air or gas. However, the term is now used for practically any product dispensed from a container by means of self-contained pressure, e.g. hair sprays, starch, shave cream, etc.

All aerosols have at least one common denominator - product is dispensed by means of a propellant acting as the force to drive the contents through the valve and out of the container. The propellant can be either a liquefied or a compressed gas, but the spray characteristics of the product depend to a considerable extent on which is used. In the case of a liquefied gas there exists a kinetic equilibrium between liquid and vapor when the pressure in the container equals the vapor pressure of the liquid phase at any given temperature. In other words, molecules are constantly leaving the liquid in the form of vapor. The accumulated molecules of vapor exert a pressure within the container and the pressure continues to increase until the pressure in the container equals the vapor pressure of the liquid at the given temperature. At that point, the number of molecules of propellant that leave the liquid phase is equalled by the number of molecules that are returned from the vapor phase to the liquid; hence, a state of equilibrium.

When the contents are dispensed, there is an increase in head space, with a resulting momentary decrease in pressure. This lowered pressure lessens the return of the molecules of propellant vapor to the liquid

phase until the pressure in the container again reaches the inherent vapor pressure. The transition takes place instantaneously, so that there is no measurable drop in pressure. Thus, with a liquified gas, the pressure inside the container remains constant as the product is used, and the spray characteristics are not significantly changed. If the propellant is dissolved in a product (commonly referred to as the "concentrate"), the same considerations apply, except that the vapor pressure is usually lower than for pure propellant, in accordance with the basic laws of physical chemistry.

In the case of compressed gases such as carbon dioxide or nitrous oxide, the situation is somewhat different, since there is no liquid phase of propellant to provide a reservoir of pressure. As the product is sprayed, the headspace inside the container increases, and the pressure decreases. At best, this is only partially offset from vaporization of the small quantity of gas dissolved in the concentrate, so that the pressure inside the container gradually drops as the product is used. Products pressurized with compressed gases usually have coarse sprays which become more so with use, and these propellants are generally used where spray characteristics are not critical (e.g., engine starters, windshield de-icers, etc.). Compressed gases have a unique advantage, however, in that their pressure does not change with temperature as much as that of the liquefied gases. For example, a container pressurized with carbon dioxide to 70 psig at 70°F. will have a pressure of approximately 65 psig at 32°F., whereas propellant 12, with a vapor pressure of 70 psig at 70°F., exerts only 30 psig at 32°F., and exerts no pressure at

all below its boiling point (-22°F.). Thus, compressed gases can be used for products at low temperatures where liquefied gases could not function.

B. Types of Aerosol Systems

Aerosols can be classified into two-phase and three-phase systems. The term "two-phase" refers to propellant vapor in equilibrium with a single-phase liquid solution of propellant and concentrate; it is commonly applied to liquefied gases, but can also include compressed gases. A three-phase system consists of propellant vapor in equilibrium with two liquid phases. A pressurized emulsion, for example, consists of a vapor phase and two liquid phases, one dispersed in the other. The propellant itself can form the nonaqueous phase of the emulsion, or it may be dissolved in the material constituting the nonaqueous phase. (All of the common propellants, with the exception of dimethyl ether, are virtually insoluble in water.)

To obtain a fine spray, it is usually necessary to use a two-phase system with a high propellant content. With such an arrangement, the mechanical atomization produced by the valve as the liquid phase passes through it is augmented by instantaneous evaporation of the propellant. The atomized droplets literally explode into smaller droplets, which form a fine spray. This fineness of spray allows a rapid and wide dispersion of product mist which tends to remain suspended in the air, in accordance with the definition of a true aerosol. Not all two-phase systems produce fine sprays, however, because low propellant content, the use of compressed gases, or large valve orifices can result in sprays of varying coarseness and wetness.

Three-phase systems usually produce coarse sprays, because the only atomization provided is that contributed mechanically by the valve.

The spray can be made finer by incorporation of a "vapor tap" (a small orifice in the valve body which allows vapor from the headspace to be mixed with the liquid stream as it flows through the passageways of the valve), or by devising a water-in-propellant emulsion, which is a means for drawing propellant into the spray. These methods produce a finer spray than could be obtained without them, but the degree of fineness is seldom near that obtainable from a two-phase system. Products such as starches, furniture polishes, or window cleaners often utilize three-phase systems with coarse (or "residual") sprays since the objective is simply to deposit the product on the surface where it is to be used. It might be noted at this point that vapor tap valves cannot be used with compressed gases because the vapor tap would permit loss of gas and, since there is no reservoir to replace that removed, the pressure will drop rapidly.

C. Propellants

The halocarbons, such as trichloromonofluoromethane and dichlorodifluoromethane, are the most widely employed propellants because of their low toxicity and complete nonflammability, but hydrocarbons (for example propane and isobutane) are also used, either alone or in combination with the halocarbons. The advantages of hydrocarbons are their comparatively low cost, resistance to hydrolysis, and low specific gravity. However, safety measures are required in the handling of hydrocarbon propellants, because they are flammable.

Compressed gases are limited to CO_2, N_2O, and N_2. Both CO_2 and N_2O are soluble in many materials. However, since CO_2 is an acid anhydride, it is not often used with aqueous products. N_2 exhibits very little solubility and has only limited application.

D. Containers

Container choice involves such considerations as product type, corrosion factors, consumer appeal, and cost. Metal cans are generally used for products that exceed 25 psig internal pressure. Two types of metal containers are available: the extruded or seamless type, which has as ICC limit of 70 psig, and the rolled or solder-seam type, which is limited to 40 psig. Tin plate and aluminum are the metals most commonly used.

In recent years, glass containers have come into prominence, particularly for cosmetic and pharmaceutical products. Glass aerosol containers are available in both uncoated and plastic-coated types. The uncoated is suitable for internal pressures up to 15 psig, and the coated for pressures up to 25 psig.

More recently, all-plastic containers molded or extruded from several types of plastic have been made available for aerosol use.

E. Valves:

Aerosol valve mechanisms are many and varied, and several hundred patents have been issued on them. The reason for such diversity is the fact that aerosol valves do much more than perform a simple on-and-off function. They must also atomize and produce a uniform spray. Although there are many variations in valve design, the basic segments are the same: an entrance orifice into the valve, an expansion chamber, and an exit orifice covered by a gasket to perform the on-and-off function. A diptube extending to the bottom of the can is attached to the entrance orifice (unless the container is to be used in an inverted position, and an actuator button is attached to the exit stem. The size of the exit orifice of the valve and actuator largely determine the degree of atomization.

Metering valves, which deliver an equal volume at each actuation, are often used with products such as pharmaceuticals and perfumes where continuous discharge is unnecessary or undesirable. Most metering valves are based on the "aerosol-within-an-aerosol" concept, where a quantity of propellant-concentrate solution is isolated in a valve chamber, and its own vapor pressure is then used to eject it. This means that two-phase, liquefied gas systems must be used, since a compressed gas or a three-phase system (except for emulsions) would not carry propellant into the isolated chamber. Metering systems for the compressed gas or three-phase system are available in the form of rising ball check valves, which are placed in the diptube, but these are not widely used.

F. Filling

Aerosol containers can be pressurized in three ways: 1) Pressure filling by forcing the propellant through the valve after the container is sealed; 2) Cold filling by chilling the propellant and other components below the boiling point and pouring them into the container before it is sealed, and, 3) "Under-the-Cap" pressure filling, wherein the valve is lifted off the container, propellant is forced under it, and the valve is then crimped on. The third method is receiving increasing acceptance in the industry, gradually displacing the more expensive cold filling technique. The first method is the most suitable when filling low concentrations of propellant.

There is a large amount of literature availble on aerosol technology. In addition to texts [1,2], trade publications such as "Aerosol Age" and "Soap and Chemical Specialties" regularly carry articles of both technical and marketing interest. Publications by suppliers to the industry are further sources of technical information.

II. PROPELLANTS

A. Fluorocarbons

The so-called fluorocarbons are halogenated derivatives of methane and ethane and are the principal propellants for the aerosol industry. The UCON fluorocarbon propellants are inert, nonflammable, non-toxic, and can meet the pressure requirements of almost any product. They are chemically and thermally stable, although the stability varies somewhat among the members of the group. Their pertinent physical properties are given in Table I.

TABLE I

Physical Properties of Ucon Fluorocarbon Propellants

Name	Ucon 11	Ucon 12	Ucon 22	Ucon 113	Ucon 114
Formula or Composition	CCl_3F	CCl_2F_2	$CHClF_2$	$CCl_2F\text{-}CClF_2$	$CClF_2\text{-}CClF_2$
Molecular Weight	137.4	120.9	86.5	187.4	170.9
Boiling Pt. at atmos. pressure					
°F.	74.8	-21.6	-41.3	117.6	38.4
°C.	23.8	-29.8	-40.8	47.1	3.6
Liquid Density-lb./gal.					
at 70°F. (21°C.)	12.4	11.1	10.1	13.2	12.3
Liquid Density-lb./cu. ft.					
at 70°F. (21°C.)	92.7	82.7	75.5	98.3	91.6
at 130°F. (55°C.)	87.6	74.4	66.4	93.2	84.9
Liquid Density-g./c.c.					
at 70°F. (21°C.)	1.49	1.33	1.21	1.58	1.47
at 130°F. (55°C.)	1.40	1.19	1.06	1.50	1.36
Solubility of Water in Ucon Propellant-% by wt.					
at 70°F. (21°C.)	0.009	0.008	.114	0.009	0.007
at 32°F. (0° C.)	0.0036	0.0024	---	0.0036	0.0026
Vapor Pressure					
at 70°F. (21°C.), psig.	---	70.1	123.3	---	12.9
Explosive Limits-% by vol. in air					
Upper	Non-Flammable	Non-Flammable	Non-Flammable	Non-Flammable	Non-Flammable
Lower					

B. Hydrocarbons

UCON isobutane, UCON propane, and their blends are odorless, non-corrosive saturated hydrocarbons. Comparatively nontoxic, they are "generally recognized as safe" by the United States Food and Drug Administration. Further, they are stable and entirely compatible with fluorocarbon propellants. UCON hydrocarbons are extremely pure in comparison to refinery stocks, which contain sulfur compounds and varying amounts of unsaturated hydrocarbons, which possess strong, characteristic odors, and which may react with other ingredients in an aerosol formulation.

The physical properties of UCON hydrocarbon propellants are given in Table II.

TABLE II

Physical Properties of Ucon Hydrocarbon Propellants

UCON Isobutane — UCON Isobutane is a colorless, easily liquefied gas. It is virtually insoluble in water, slightly soluble in alcohol, and quite soluble in ether. It is shipped as a colorless, liquefied gas under its own vapor pressure of 30.7 psig at 70°F.

UCON Propane — UCON Propane is a gas at atmospheric pressure and normal temperatures and is colorless in both its gaseous and liquid phases. It is soluble in ether and alcohol, and virtually insoluble in water. Propane is shipped as a liquefied gas under its own vapor pressure of 110 psig at 70°F.

PHYSICAL PROPERTIES

	UCON Isobutane	UCON Propane
Formula	C_4H_{10}	C_3H_8
Molecular Weight	58.120	44.094
Boiling Point at 14.696 psia	10.9°F.	-43.7°F.
Freezing Point at 14.696 psia	-255.3°F.	-305.8°F.
Specific Gravity, Liquid, at 60/60°F.	0.5631	0.5077
Weight/Gal., Liquid, at 60°F.	4.685 lb.	4.224 lb.
Specific Gravity, Gas, (Air = 1)	2.066	1.522
Volume of Vapor/Lb., at 60°F. and 14.696 psia	6.339 cu. ft.	8.471 cu. ft.
Volume of Vapor/Gal. Liquid, at 60°F. and 14.696 psia	29.70 cu. ft.	35.78 cu. ft.
Ratio, Gas Volume/Liquid Volume at 60°F. and 14.696 psia	222.1	267.6
Critical Temperature	275.0°F.	206.3°F.
Critical Pressure	529 psia	617 psia
Autoignition Temperature	1010°F.	874°F.
Coefficient of Liquid Expansion at 60°F.	0.0012	0.0016
Solubility in Water in, at 70°F.	0.0073% by wt.	0.016% by wt.
Solubility in Water at 70°F.	0.0085% by wt.	0.007% by wt.
Surface Tension at 70°F.	10.05 dynes/cm.	7.0 dynes/cm.
Toxicity, U. L. rating system	5.	5.

TABLE II (continued)

UCON Blend (90-10)	UCON Blend (90-10) is a combination consisting of 89.5 per cent isobutane and 10.5 per cent propane, by weight. This special blend complies with the Interstate Commerce Commission Regulations, Tariff No. 13, Article 73.302(a) (3), for regular metal containers, filled to a pressure not in excess of 55 psia at 70°F. UCON Blend (90-10) is shipped as a liquefied gas under its own vapor pressure of 40 psig at 70°F.
UCON Blend (84-16)	UCON Blend (84-16) is a combination consisting of 84.1 percent isobutane and 15.9 per cent propane by weight. This blend has a vapor pressure of 46 psig at 70°F.

PHYSICAL PROPERTIES

	UCON Blend (90-10)	UCON Blend (84-16)
Weight Per Cent, Isobutane	89.5	84.1
Weight Per Cent, Propane	10.5	15.9
Mol Per Cent, Isobutane	87	80
Mol Per Cent, Propane	13	20
Liquid Volume Per Cent, Isobutane, at 70°F.	88.5	82.7
Liquid Volume Per Cent, Propane, at 70°F.	11.5	17.3
Specific Gravity, Liquid, at 60/60°F.	0.557	0.554

C. Dimethyl Ether and Vinyl Chloride

Dimethyl ether and vinyl chloride are not used by themselves to any great extent, but they are used in mixtures as discussed below. Their physical properties are listed in Table III.

TABLE III

Physical Properties of UCON Vinyl Chloride and UCON Dimethyl Ether

Name	UCON Vinyl Chloride	UCON Dimethyl Ether
Formula or Composition	CH_2=CHCl	CH_3-O-CH_3
Molecular Weight	62.5	46.1
Boiling Point at atmospheric pressure		
°F.	7.0	-11.0
°C.	-13.4	-23.7
Liquid Density-lb./gal.		
at 70°F. (21°C.)	7.6 (*)	5.5 (*)
Liquid Density-lb./cu. ft.		
at 70°F. (21°C.)	56.9 (*)	41.2 (*)
at 130°F. (55°C.)	---	---
Liquid Density-g./c.c.		
at 70°F. (21°C.)	0.912 (*)	0.661 (*)
at 130°F. (55°C.)	---	---
Solubility of Water in UCON Propellant-% by wt.		
at 70°F. (21°C.)	0.09	---
at 32°F. (0°C.)	---	---
Vapor Pressure at 70°F.		
(21°C.), psig.	35	60
Explosive Limits-% by vol. in air		
Upper	21.0	18.1
Lower	4.0	3.5

(*) At 20°C.

D. Specialty Blends

Union Carbide pioneered the development of economical mixtures of fluorocarbons with lower-cost flammable gases, arriving at blends that are still nonflammable and can be used without extensive safety systems in filling plants and with no inherent hazard to consumers. The technology of propellant blends has been published[3,4,5] and is reproduced in Appendices A, B, and C.

The blends were designed on the basis of pressure so as to serve broad areas of application--a high-pressure mixture to substitute for propellant 12 in products such as paints, moderate-pressure blends for low-viscosity, alcohol-type products, and a low-pressure blend for glass bottle items such as perfumes and colognes. Based on techniques used by the Bureau of Mines[6], four standard mixtures were devised, with the properties shown in Table IV. They can all be used with the same equipment as for fluorocarbons.

TABLE IV

Physical Properties of UCON Specialty Blends

Name	UCON Fragrance Propellant	UCON Vinyl Chloride Propellant	UCON Propellant A	UCON Paint Propellant
Formula or Composition	82.3% UCON 114 9.2%UCON12 8.5%Butane	39%UCON 11 39%UCON 12 22% Vinyl Chloride	45%UCON 11 45%UCON 12 10%Isobutane	15% Dimethyl Ether 75% UCON 12 10% UCON 11
Molecular Weight	---	---	---	---
Boiling Point at atmospheric pressure				
°F.	---	---	---	---
°C.	---	---	---	---
Liquid Density-lb./gal.				
at 70°F. (21°C.)	11.5	10.5	10.6	10.1
Liquid Density-lb./cu. ft.				
at 70°F. (21°C.)	86.1	78.6	79.2(*)	75.5
at 130°F. (55°C.)	---	---	---	---
Liquid Density-g./c.c.				
at 70°F. (21°C.)	1.38	1.26	1.27(*)	1.21
at 130°F. (55°C.)	---	---	---	---
Solubility of Water in UCON Propellant-% by wt.				
at 70°F. (21°C.)	---	---	---	---
at 32°F. (0° C.)	---	---	---	---
Vapor Pressure at 70°F. (21°C.), psig.	20	36.5	38	62
Explosive Limits-% by vol. in air				
Upper Lower	Non-Flammable	Non-Flammable	Non-Flammable	Non-Flammable

(*) At 77°F.

1. UCON Fragrance Propellant is a substitute for propellant 12/114 10/90, often used for aerosol perfumes and colognes. Butane is used as the low-cost blending agent, and the resulting mixture is comparable in performance with the straight fluorocarbons. It is suitable for use with uncoated glass containers as well as other aerosol packages.

2. UCON Vinyl Chloride Blend is a moderate-pressure blend that can be substituted for propellant 12/11 50/50. It is competitive in performance and economy with the fluorocarbons and is particularly suitable for insecticides, room deodorants, and other products utilizing moderate-pressure propellants.

3. UCON Propellant A is also a moderate-pressure blend that can be substituted for propellant 12/11 50/50. Repeated laboratory tests and field experience have verified its adaptability to a variety of products, and it can be used in the same manner and with the same equipment as any of the UCON Fluorocarbon Propellants.

4. UCON Paint Propellant is a high-pressure mixture designed as a substitute for propellant 12 and is so named because its principal application is in aerosol paints. It can generally be used, however, with any product that would use propellant 12.

Occasionally a pressure is desired which falls in a different range from that of the standard blends. This is often the case when other ratios than 50/50 of propellant 12 and 11 are being used. It is possible to adjust the composition of a standard blend to duplicate the desired pressure, and the calculations are given in Appendix D. It should be noted that this usually involves a reduction in the concentration of the flammable component; i. e., the concentration of the flammable component cannot be held constant while the fluorocarbon ratios (*) are varied at will.

Charts showing vapor pressure and density versus temperature relationships for selected blends are given in Appendix E, F, G, H, I, J, K, and L.

(*) See explanation in Reference 1

E. Azeotropes

All of the propellant blends discussed above exhibit fractionation when exposed to evaporative conditions. For this reasons, they contain less than the theoretically allowable concentration of the flammable component to maintain safety in spite of fractionation. An azeotrope does not fractionate, however, and in the case of azeotropes of the fluorocarbons with other compounds there is no "head and tail" requirement, assuming the mixture itself to be nonflammable. A definitive study of azeotropes has been published and is reproduced in Appendix M.[7] Only two azeotropes are listed which are deemed suitable for aerosol use, both based on UCON propellant 114 and serving the same function.

I. Binary Azeotrope

Ethyl Chloride	=	17%
UCON Propellant 114	=	83%

II. Ternary Azeotrope

UCON Propellant 21	=	7.8%
Ethyl Chloride	=	8.5%
UCON Propellant 114	=	83.7%

Of the two, the binary mixture is the more economical and has advantages as a substitute for propellant 114, particularly in perfumes and colognes.

F. Compressed Gases

The comparatively low cost of the compressed gases makes them attractive as aerosol propellants. However, their limited solubility, and the fact that all aerosols pressurized with them experience a pressure drop as the product is dispensed, keep the compressed gases from being the solution to all propellant problems. In spite of these drawbacks, there are many aerosol applications for carbon dioxide, nitrous oxide, and nitrogen. A list of their physical properties is given in Table V, and solubility data is shown in Table VI.

TABLE V

Physical Properties of Compressed Gas Propellants

	Carbon Dioxide	Nitrous Oxide	Nitrogen
Chemical Symbol	CO_2	N_2O	N_2
Molecular Weight	44.010	44.016	28.016
Specific Gravity (Air = 1) 70°F., 1-ATM	1.5292	1.532	0.9670
Density LB./CU. FT. 70°F., 1-ATM	0.1146	0.1148	0.07247
Specific Volume cu. ft./lb. 70°F., 1-ATM	8.729	8.711	13.80
Normal Boiling Point, °F.	-----	-127.3	-320.45
Sublimation Temperature, °F.	-109.17	-----	-----
Latent Heat of Evaporation, BTU/lb.	-----	161.78	85.67
Critical Pressure, Atmospheres, Abs	72.292	71.70	33.49
Critical Pressure, lbs./sq.in., Abs	1071.7	1053.7	492.2
Critical Temperature, °F.	+88.410	-97.700	-232.870
Triple Point Temperature, °F.	-69.884	-131.456	-346.027
Specific Heat, Constant Pressure, 70°F.	0.2016	0.2095	0.2484
Specific Heat, Constant Volume, 70°F.	0.1543	0.1609	0.1774
Color	None	None	None
Odor	None	None	None
Taste	None	Slight (Sweet)	None

TABLE VI

Solubility* of Compressed Gas Propellants in Various Solvents

	Carbon Dioxide	Nitrous Oxide	Nitrogen
Water	0.82	0.6	0.016
Acetone	6.3	5.3	0.15
Acetic Acid	4.7	4.5	0.12
Pyridine	3.6	3.4	----
Methyl Alcohol	3.8	3.2	0.14
Ethyl Alcohol	2.6	2.8	0.14
Benzaldehyde	2.8	3.0	-----
Aniline	1.3	1.4	0.03
Amyl Acetate	4.1	4.9	0.15
Ethylene Bromide	2.1	2.7	----
Isoamyl Alcohol	1.8	2.4	----
Chloroform	3.4	5.2	0.13
Cyclohexanol	----	0.23	----
Glycerol	0.03	1.20	----
Carbon Disulfide	0.87	----	0.06
Nitrobenzene	----	----	0.06
Benzene	2.40	----	0.12
Xylene	2.15	----	0.12
Toluene	1.80	----	0.12
Amyl Alcohol	2.30	----	0.12
Ethyl Acetate	----	----	0.17
Isobutyl Acetate	----	----	0.17
Methyl Acetate	6.5	----	0.18
Carbon Tetrachloride	4.15	4.28	0.148
Petroleum Distillates	----	2.10	0.109
Ethylene Chloride	3.23	3.20	----
Isobutyl Chloride	2.84	----	----
Mineral Oil	----	----	0.071
Heavy Naphtha	----	----	0.10

* Bunsen Coefficient: The solubility coefficient is defined as the number of ml. of gas, reduced to $0^{o}C$. and 760 mm of mercury, dissolved by one ml. of solvent at 1 atm and the designated temperature. The units of solubility are ml. gas (STP)/ATM-ml. liquid. To find the volume (standard conditions) of gas dissolved at any other pressure, the solubility coefficient is multiplied by the pressure in atmospheres. The reliability of measurements is estimated to be $\pm$ 5% for a solubility coefficient of 1.0.

III. WATER-BASED SYSTEMS

Water-based space sprays, in contrast to the residual-type products such as starches and polishes, are relatively new to the aerosol field, but they are receiving increasing attention. They consist of water-in-oil (w/o) emulsions with the propellant as the external phase. This arrangement provides a finer spray than could be obtained by an oil-in-water (o/w) emulsion, and hydrolysis problems are minimized since water forms the internal phase. An experimental program on water-based space sprays was carried out in the UCON Propellants Laboratory and the work has been published[8]. This discussion appears in Appendix N.

The following formulations were found to produce relatively fine sprays and are suggested as starting points for developing aqueous space spray products:

	Concentration, % by weight	
Component	I	II
Light Mineral Oil ("Isopar M," "Shell Sol 71," etc.)	10%	5%
Emcol 14	1%	1%
Deionized Water	44%	46%
UCON Propellant 12/Isobutane 30/70	45%	--
UCON Propellant 12/Isobutane 25/75	--	48%

IV. FORMULATIONS

Aerosol products are as varied as the chemical specialties industry itself and, as a result, their formulation encompasses a wide range of materials and combinations. The type of system, components, valve, and container to be used depend upon the product and what it must do. If a fine spray is desired, a two-phase system with a high propellant content would be the logical starting point, with a small exit orifice in the valve and possibly a mechanical breakup actuator. If a coarse, wet spray is preferable, the propellant content could be lowered or a three-phase system could be chosen, especially if water is present. If maintenance of pressure at low temperatures is critical, as would be the case with an engine starting fluid, a compressed gas would be required. In the case of foams, the stability and stiffness of the foam will depend greatly on the propellant used and its concentration. These are examples of some of the factors that the aerosol chemist must deal with in formulating his products, and they can be pictured graphically by the following "trend curves" (Figures 1 and 2). The curves do not represent experimental data but show the qualitative relationships between formulating variables.

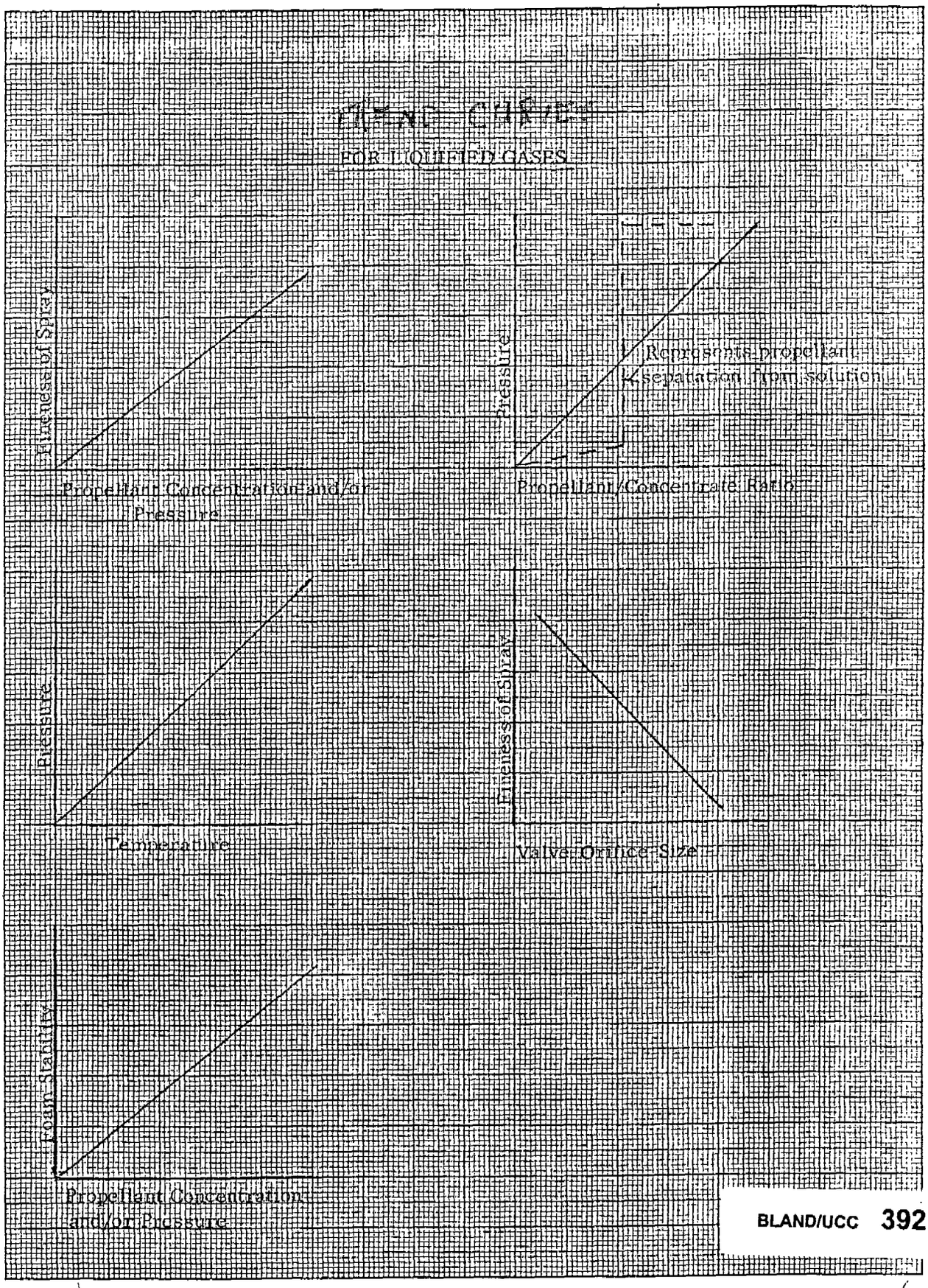
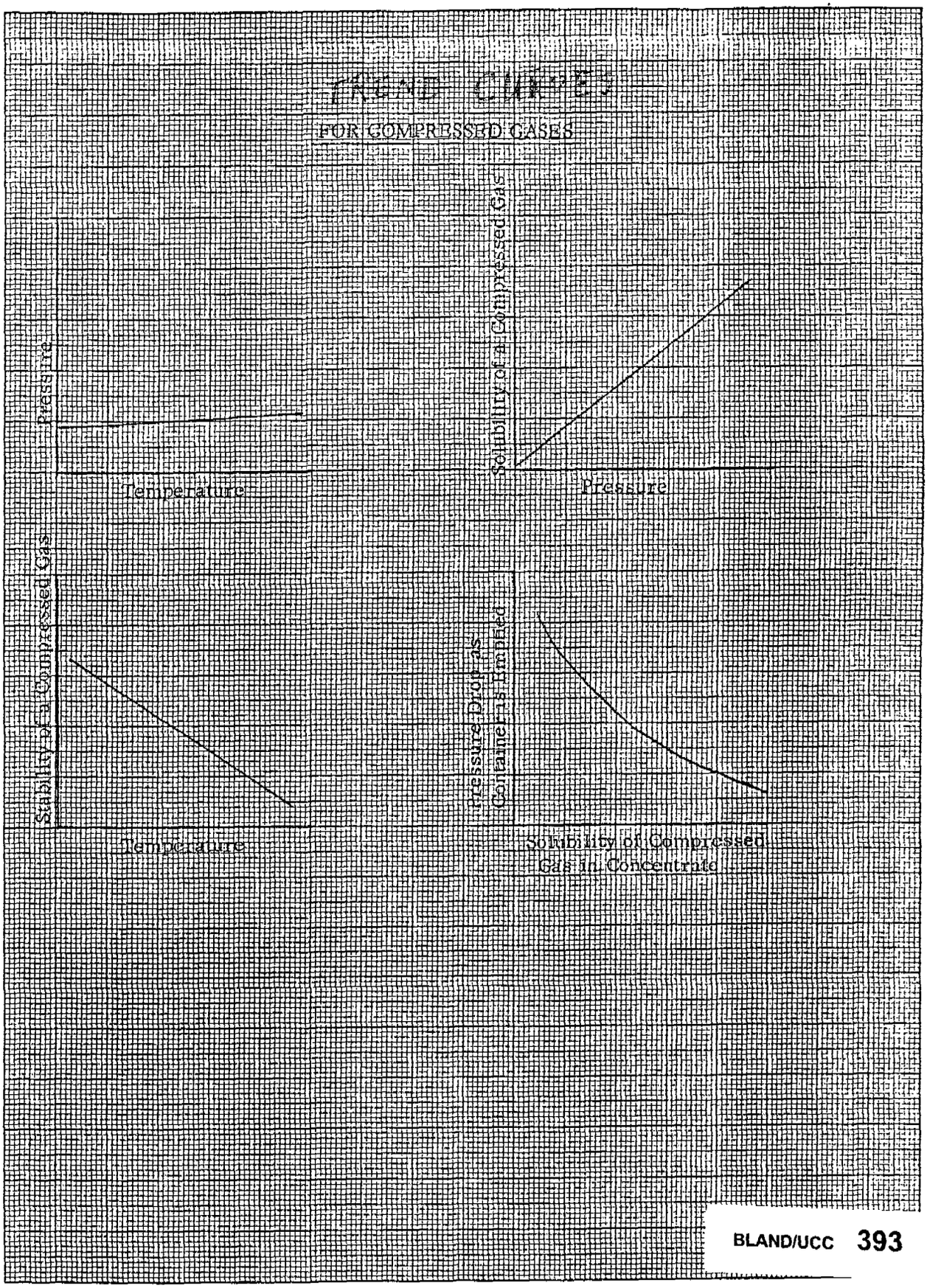


Figure 1.



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BLAND/UCC 393

Figure 2.

As a general rule, the higher the pressure inside an aerosol container and the higher the propellant content, the finer will be the spray. There are limitations to the container pressure, however, and it is often necessary to use mixtures of propellants to obtain the best results. UCON propellant 12 has a pressure of 70 psig at 70°F. (Table I), and if dilution with the concentrate does not lower the pressure below ICC limits, some of the propellant 12 will have to be replaced with a higher boiling material such as propellant 11 or 114. A common mixture in wide use is propellant 12/11 50/50, although many other ratios can be utilized. If water is present in the formulation, propellant 114 should be used instead of 11, since the latter is susceptible to hydrolysis and may cause corrosion problems. Hydrocarbon propellants are also used with water-based products because they do not hydrolyze and the presence of water suppresses their flammability.

When three-phase, water-based systems are used, the specific gravity of the propellant becomes important. Hydrocarbons, with their low density, float on top of the aqueous phase, which allows the use of a vapor tap valve to assist in providing breakup to the spray. High-density fluorocarbons, on the other hand, sink below the aqueous phase and their vapor must bubble up through it to provide pressure in the headspace. This causes erratic behavior of the spray, especially with vapor tap valves, and for this reason hydrocarbons are generally preferred for three-phase, water-based products. A method for utilizing this system for space sprays was mentioned previously[8].

Aerosol foams are emulsions, and the foam characteristics depend on a number of factors, including the type of emulsion itself, i.e., whether it is a water-in-oil (w/o) or an oil-in-water (o/w) emulsion. Products such as furniture polishes, window cleaners and shave creams are usually o/w emulsions, with the propellant dissolved in the oil phase or itself forming the oil phase. They can be ejected as a foam by use of special foam valves, although the first two are usually applied as a coarse spray. In the case of shave-cream-type foams, the higher the propellant content the more stable and drier the foam will be. Conversely, low propellant contents usually produce wet, running foams. Other factors, of course, influence foam characteristics, and the presence of polymeric thickeners, for example, will contribute greatly to stability. Quick-breaking foams can be obtained by adding alcohol and defoamants.

Presented below is a group of formulations representative of various types of products and propellant systems. They are suggested as starting points from which finished products can be developed. All have passed limited storage stability tests, but their suitability for the market should be verified. A large number of formulations are also on file in the UCON Propellants Laboratory and are available on request.

A. Adhesive

The following formulation produces a coarse spray which is desirable for a pressure-sensitive adhesive. A finer spray can be obtained by reducing the resin content and increasing the methylene chloride. The sprayed coating should be allowed to dry for about 30 seconds before cementing the surfaces.

Component	Concentration, %
"Vistanex" LMMH Polymer (Enjay Chemical Company)*	4.0
Methylene Chloride	46.0
UCON Propellant 12	50.0

Valve Orifices = .080" x .018"

Actuator = .018"

*The polymer can be modified by addition of other resins to obtain specific properties desired -- see literature available from Enjay Chemical Company.

B. Dust Mop Spray

The active component of a dust mop spray is usually a light mineral oil. The oil can either be packaged in an anhydrous system with a fluorocarbon, or incorporated into an aqueous emulsion and packaged with a hydrocarbon propellant, as shown by the following two formulations:

	I	II
Mineral Oil	50%	40%
Oleic Acid	--	10%
Triethanolamine	--	3%
Deionized Water	--	25%
UCON Propellant 12	50%	--
UCON Isobutane	--	22%

Mixing Procedure for Formulation II: Add oleic acid to mineral oil and triethanolamine to water. Add the oil to the water slowly with stirring. Package in the usual manner.

Valve Orifices = .080" x .018"

C. Foam for Pharmaceuticals

The use of aerosol foams as carriers for medicinal products has received increasing attention from pharmaceutical marketers. Convenience of application, sterility, and maintenance of biological activity are among the numerous advantages. Since aerosol foams are emulsions, however, the usual difficulties of gelling or phase separation are often encountered. Particularly troublesome are those products involving cationic materials, which require specific surfactants to form stable emulsions.

Listed below are two formulations that exhibit long-term stability with cationic pharmaceuticals. Both have been packaged with varying amounts of propellant to produce foams of different types, from a very wet to stiff and dry. The texture of the foams produced by the "Polawax" formula may be a little more preferable than those of glycerol monostearate, but the ultimate choice will depend on the intended applications and compatibility with active ingredients.

Part A	I	II
Glycerol Monostearate	2.5%	--
"Polawax"	--	2.5%
Cetyl Alcohol	1.0%	--
Glycerine	--	5.0%
"Span" 80	0.5%	0.5%
Part B		
"Atlas" G-271	3.5%	3.5%
"Sorbo"	5.0%	--
Deionized Water	87.5%	88.5%

Mixing Procedure: Parts A and B are mixed separately, heated to 80-90°C., and then combined with stirring until cool.

Package:		I	II
Concentrate	=	96%	90%
UCON Propellant 12/114 20/80	=	4%	10%

D. Flowering Fertilizer

It has been shown by radioactive tracer techniques that plant feeding through the foliage can be more effective than feeding through the root system[8]. The nutrients used for this purpose are so-called soluble fertilizers, i.e., water-soluble salts containing the elements nitrogen, phosphorus, and potassium. A solution of these salts in an aerosol container offers convenience both from the standpoint of storage and elimination of mixing of the salts each time they are to be used.

It is generally preferred to have separate fertilizers for flowering and nonflowering plants. The two formulations below evolved from tests conducted on a number of plant species that responded with increased lustre and vigor, rather than growth -- a desirable feature for indoor plants:

Flowering Plants(*)		Nonflowering Plants(*)	
(Should not be sprayed directly on blooms)			
Ammonium Nitrate	= 2.00 Parts	Potassium Nitrate	= 44.00 Parts
Potassium Nitrate	= 1.00	Ammonium Sulfate	= 6.00
Diammonium Phosphate	= 0.75	Urea	= 10.00
Calcium Sulfate	= 0.25	Triple Superphosphate	= 15.00
Ferrous Sulfate	= 0.25	Calcium Carbonate	= 0.04
Ammonium Chloride	= 0.25		

(*) Dry Mix Basis

Mixing Procedure: Dry Powder Mix 0.5 gms. . . . . 0.25 gms.
Sterile Water . . . . . 1 liter

Package:		
Concentrate	=	95%
UCON Propane/Isobutane 10/90	=	5%
Valve Orifices	=	.013" - 2 x .020"
Actuator	=	Mechanical Breakup

E. Furniture Polish

Furniture polishes generally consist of oil-in-water emulsions that remove both oil- and water-soluble soils and impart a good lustre to the finish. Some products incorporate waxes to increase protection a durability of the polish, while others use only an oil that imparts a high sheen for a shorter time. The following formulation can be varied in these respects to obtain the desired properties:

UNION CARBIDE Silicone L-45, (350 cs.)	1.250%
"Crown" Wax 23	1.025%
Carnauba Wax No. 1	1.025%
"Hystrene" T-70	1.375%
"Sovasol" No. 5	12.000%
Deionized H_2O	82.500%
Triethanolamine	0.825%

Mixing Procedure: Heat the L-45,waxes, and "Hystrene" T-70 over a steam bath to 195°F. until the waxes are melted. Heat the water to boiling, and add the triethanolamine. Gradually, with rapid stirring, add the triethanolamine-water solution to the hot wax solution. Stir until the emulsion reaches 113°F., and add the "Sovasol". Continue stirring until the emulsion is cool.

Package: Concentrate = 95 - 90%

UCON Propellant 12/114, 40/60 or UCON Isobutane = 5 - 10%

F. Hair Spray

Hair sprays are the largest selling aerosol product. They consist of a resin and resin modifiers, alcohol, perfume, and propellant. The following is a typical formulation, but there are many variations, particularly in regard to the resin, in use today:

PVP/VA 60/40	3.0%
Dibutyl phthalate	0.5%
Perfume	0.2%
UNION CARBIDE Silicone L-45 (100 cs.)	0.1%
UCON Aerosol Alcohol (SDA-40)	25.2%
UCON Propellant 12/11 40/60	70.0%

G. Hand Cleaner and Ink Stain Remover

"Waterless" hand cleaners have been available for several years in both aerosol and conventional packages. An interesting improvement in these products can be made by incorporating components that will remove ink stains. Surfactants have to be carefully chosen, however, for some ink-removing ingredients, such as sodium meta-bisulfite, can cause discoloration, precipitation, and emulsion instability. Anionic surfactants, and particularly triethanolamine stearate, provide satisfactory foams with or without the bisulfite, as shown by these formulations:

	I	II
Stearic Acid	3.5%	5.0%
Triethanolamine	2.0%	2.7%
Polyethylene Glycol 600-Distearate	5.0%	5.0%
Lanolin	3.0%	3.0%
Propylene Glycol	7.5%	7.5%
CARBITOL® Solvent	7.5%	7.5%
Sodium Meta-bisulfite	3.0%	----
Deionized Water	67.5%	68.3%
Perfume	1.0%	1.0%

Mixing Procedure: Melt the stearic acid and lanolin and add the CARBITOL® solvent and propylene glycol. Heat the water, triethanolamine, and distearate, and add to the other mixture. Cool with stirring to 40°C., add the sodium meta-bisulfite and perfume, and cool to room temperature with stirring.

Package: Concentrate = 96%
UCON Propellant 12 = 4%

Valve: "Clayton" standard flow foam valve.

H. Paint Brush Conditioner and Preservative

The UCON polyalkylene glycols are solvents for many paints and make good conditioning agents for storage of paint brushes between periods of use. Both the UCON fluid LB and 50-HB series are suitable, although the latter is preferred, since it is compatible with both oil- and water-based paints, and the brush can be put to use without wiping or rinsing. UCON fluid 50-HB-260, when packaged as shown below, produces a coarse spray that deposits as a quick-breaking foam, and the fluid penetrates rapidly into the fibers of the brush. For long storage periods, a cover or wrapping should be used to prevent drying out of residual paint on the brush.

UCON Fluid 50-HB-260	=	35%
Isopropanol	=	15%
UCON Propellant 12	=	50%

Valve Orifices = .018" x .018"

Actuator = .018"

I. Personal Deodorant

An aerosol personal deodorant consists of an antiperspirant agent, perfume, cosolvent (usually alcohol), and propellant. Auxiliary agents such as a bactericide and glycols are sometimes incorporated. The finished product should have a fast-drying spray that produces a nontacky, nonflaking deposit:

Perfume	=	0.25%
Hexachlorophene	=	0.25%
Aluminum Sulfocarbolate	=	2.00%
UCON Aerosol Alcohol (SDA-40)	=	62.50%
UCON Propellant 12	=	35.00%

Valve Orifices	=	.016" x .0135" with .016" vapor tap
Actuator	=	.060" MB

J. Quick-Breaking Foam

Although stable foams are usually desired and not always easily obtained, it is sometimes preferable to dispense a product as a quick-breaking foam which yields a rapidly spreading liquid film. The following mixture provides a fast-breaking foam that leaves no soap-like residue, and the degree of stability can be varied to meet the various requirements of different products. Increasing the surfactant and decreasing the alcohol produces a more stable foam, and the reverse makes for a more rapidly breaking foam:

UCON Aerosol Alcohol (SDA-40)	=	38%
Deionized Water	=	53%
"Onyxol" 336	=	2%
"Glycosperse" O-20	=	2%
UCON Propellant 12/114 20/80	=	5%

Valve: Optional, depending on the type of foam ejection desired.

K. Spray Starch

One of the largest-volume aerosol products, spray starches have received increasing acceptance because of their convenience and time-saving features. The following is a formulation that is adaptable to various valve and actuator arrangements to provide the specific spray pattern and fabric wetting desired:

Starch Solution (4 per cent Corn Products Company B-771)	89.25%
Isopropanol	5.00%
Hexachlorophene	0.25%
Methyl Parasept	0.25%
Propyl Parasept	0.25%
UCON Propane/Isobutane 10/90	5.00%

Mixing Procedure: Mix starch with water and allow to stand overnight. Heat to 98°C. and stir to disperse starch. When cool, add the preservatives dissolved in isopropanol. Homogenize the mixture and package it.

L. Touch-Up Floor Polish

Standard latex floor polishes can be pressurized with nitrous oxide to provide a means for renewing worn or spotted floor areas between periods of regular polishing. Application of the product as a spray followed by manual spreading gives the best results:

Latex Polish (Polyvinyl Chemicals CW-1 or UBS Chemical Co. RHW-0424-3)	= 100%
Nitrous Oxide	= to 105 psig at 70°F.
Valve Orifices	= 0.100" x .030"
Actuator	= Mechanical Breakup

M. Wax for Wood Floors

A polymer for use in polishes for wood floors is supplied by Polyvinyl Chemicals,Incorporated, as "Neocryl" B-705. The polymer is reported to form "dry-bright" polishes in combination with conventional waxes and resins but, unlike conventional polishes, dries to a gloss without buffing. This makes the product attractive for aerosol packaging, since full advantage can be taken of the convenience of spray application without the need for mops and buffers, or the labor associated with polishing conventional waxes. The polymer is incorporated into a concentrate designated WP-70 by Polyvinyl Chemicals, details of which are available from the supplier. Aerosol packaging consists of:

WP-70 Concentrate		=	60%
UCON Propellant 12/11	50/50 or Propellant A	=	40%
Valve Orifices	= .080" x .018"		
Actuator	= .016"		
Container	= Unlined, sideseam tinplate		

N. Window Cleaner

Window cleaners must remove not only dirt and dust but also grease-like soils. This requires a mixture of both solvents and surfactants, and accounts for the wide variety of such cleaners on the market. It is generally desirable not to leave a film after the cleaner is used, but surfactants, which constitue a good part of the residual film, are necessary for effective soil removal. The following mixture represents a balanced combination which is efficient and leaves essentially no film:

TERGITOL NPX	=	0.3%
Ammonia (28% Aqueous)	=	1.0%
Isopropanol	=	35.0%
Deionized Water	=	60.0%
UCON Propellant 12/114 35/65		
or		
UCON Isobutane	=	4.0%

Valve Orifices	=	.100" x .030"
Actuator	=	MB
Container	=	Tinplate, phenolic lined

V. THE AEROSOL LABORATORY

Very little specialized equipment is required for an aerosol laboratory. Two items that are essential, however, are a crimper and a pressure filler. These are used for sealing and pressurizing the container and are available from Aerosol Machinery Company, Westbury, New York; Builders Sheet Metal Works, Inc., New York, New York; Colton Kiefer Division, Cedar Rapids, Iowa; and General Kinetics, Inc. Atlanta, Georgia.

Other equipment is mostly optional but often very helpful. Glass compatibility tubes such as those supplied by the Fischer & Porter Company provide visual observation of what happens when propellant and product are mixed and, when properly handled, are safe to use for this purpose. Cold filling can be accomplished with a conventional freezer by immersing a coil of copper tubing in an aqueous glycol bath in the bottom of the freezer. The tubing is attached at one end to a cylinder of propellant outside the freezer and to a valve at the other end. As propellant is drawn through the coil it is cooled below its boiling point and is ready for cold filling.

A supply of representative valves is convenient, although the extent of the inventory will depend on the number and type of products being handled. The same applies to a container inventory. If glass bottles are to be filled, a spin-type crimper will be necessary for them, since glass-bottle valves are different from metal-container valves.

Hoses, connectors, pressure gauges and valves for transferring propellant from storage cylinders to filling equipment are available from the suppliers listed above. In addition, each October issue of Aerosol Age contains a buyer's guide for the aerosol industry where a supplier for almost any piece of aerosol equipment can be found.

Beyond this, standard items such as are found in any laboratory will be necessary. Requirements for scales, balances, pH meters, ovens for storage testing, chemicals (particularly formulating materials), gas chromatographs and other analytical instruments will depend on the function and scope of laboratory activities.

VI. PRELIMINARY DESIGN OF AN AEROSOL FILLING LINE

INTRODUCTION

This section describes a general approach to the design of facilities for filling aerosol containers. Although equipment sizing and construction details will vary with the specific product being handled and the volumes involved, the approachdescribed below will be useful for reference. The recommendations that follow cover receipt of raw materials, mixing, the filling line itself, warehousing and services, operating labor requirements, estimates of investment, and typical layouts. The purpose is to describe all equipment required to produce a finished product ready for shipment. Should a filler plan to use an existing building or existing storage tanks, the investment can be adjusted without difficulty.

DESIGN BASIS

Filling facilities are designed for an annual rate of 12,500,000 units (50,000/day) on the basis of one-shift operation and a 250-day year. The container is assumed to be a 211 x 413 can (12-ounce size) with an 11-ounce fill. The recommended equipment will handle smaller containers (down to 202 x 214 cans) with no decrease in units filled per minute. Larger containers can also be handled, although it might be necessary to reduce line speed if a large propellant charge is required.

For general discussion, we assume a product which is 40% by weight concentrate and 60% by weight propellant, with the propellant being a pre-mixed blend of UCON Propellant 12/11 50/50. In selecting materials of construction, the concentrate was considered to be similar to a lower alcohol such as ethanol or isopropanol. The design is based on a concentrate blend of 90% alcohol and 10% other components and additives.

The facilities described here are designed to package one base product. However, minor variations (such as the three resin concentrations normally used in hair sprays or the varied fragrances added to room deodorants) can be handled easily. A highly flexible facility for packaging widely varying products would require changes, primarily in the bulk storage and mixing areas. These changes could be handled without difficulty within the general framework described here.

The case-packing and finished-product handling system are based on cartons of 12 cans. Provision is made for the special packs and deals which are common in consumer product marketing.

The facilities are designed as a completely new installation in a separate building with no constraints from adjacent structures and existing operations. Such factors must be considered in final planning, but they are not included in this study. In fact, treating the facility as an independent unit clarifies the incremental investment needed for service facilities, warehousing, and the like.

Being a new facility, the unit can take advantage of the latest developments in aerosol technology. Such improvements as automatic valve-placing and high-speed gassing with the actuator button in place were impossible until recently. Although the facility is specifically designed for filling one basic product, flexibility for handling other materials has been included wherever this could be done without affecting the cost.

The recommendations are based on published data and on experience. They should be used for estimating purposes only, since specific proposals must depend on the needs of the individual filler. The suggested unit

would consist of a single high-speed filling line installed in a new building. We estimate the complete cost of a suitable installation at about $325,000, based on mid-1963 prices (Table VII). In the sections following, each major part of the proposed facility is covered in detail along with a brief discussion describing the method of operation and the reasons for our recommendations.

(Table VII)

BUILDING

As shown on the attached plot plan of the proposed facility (Figure 3), we would recommend a building 140 feet long and 105 feet wide with a total floor area of 15,300 square feet, including a small mezzanine. The building would have a structural steel frame with masonry or insulated metal walls and an insulated roof with a clear height of at least 17 feet. Truck docks would be provided as shown on the drawing. To accommodate future expansion, the building can be extended to the north.

(Figure 3)

Table VII

Summary of Investment

Building		$135,000
Bulk Storage		
Alcohol tank	$ 8,000	
Propellant tank	9,300	
Sub-total Bulk Storage		17,300
Mixing		24,100
Filling Line		
Unscrambler	2,900	
Can-cleaner	1,800	
Can-coder	600	
Concentrate filler	6,900	
Valve-inserter	11,600	
Crimper	16,200	
Gasser	19,000	
Water bath	10,800	
Overcapper	5,600	
Labeler	4,400	
Case-sealer	4,900	
Case-coders	300	
Conveyors	15,000	
In-line quality control	1,000	
Installation	15,000	
Sub-total Filling Line		116,000
Auxiliaries		
Boiler	5,500	
Air-compressor	10,000	
Lift trucks	7,800	
Laboratory equipment	3,500	
Shop equipment	1,500	
Locker room and miscellaneous equipment	1,500	
Sub-total auxiliaries		29,800
Total (Excluding Engineering and Contingencies)		$322,200

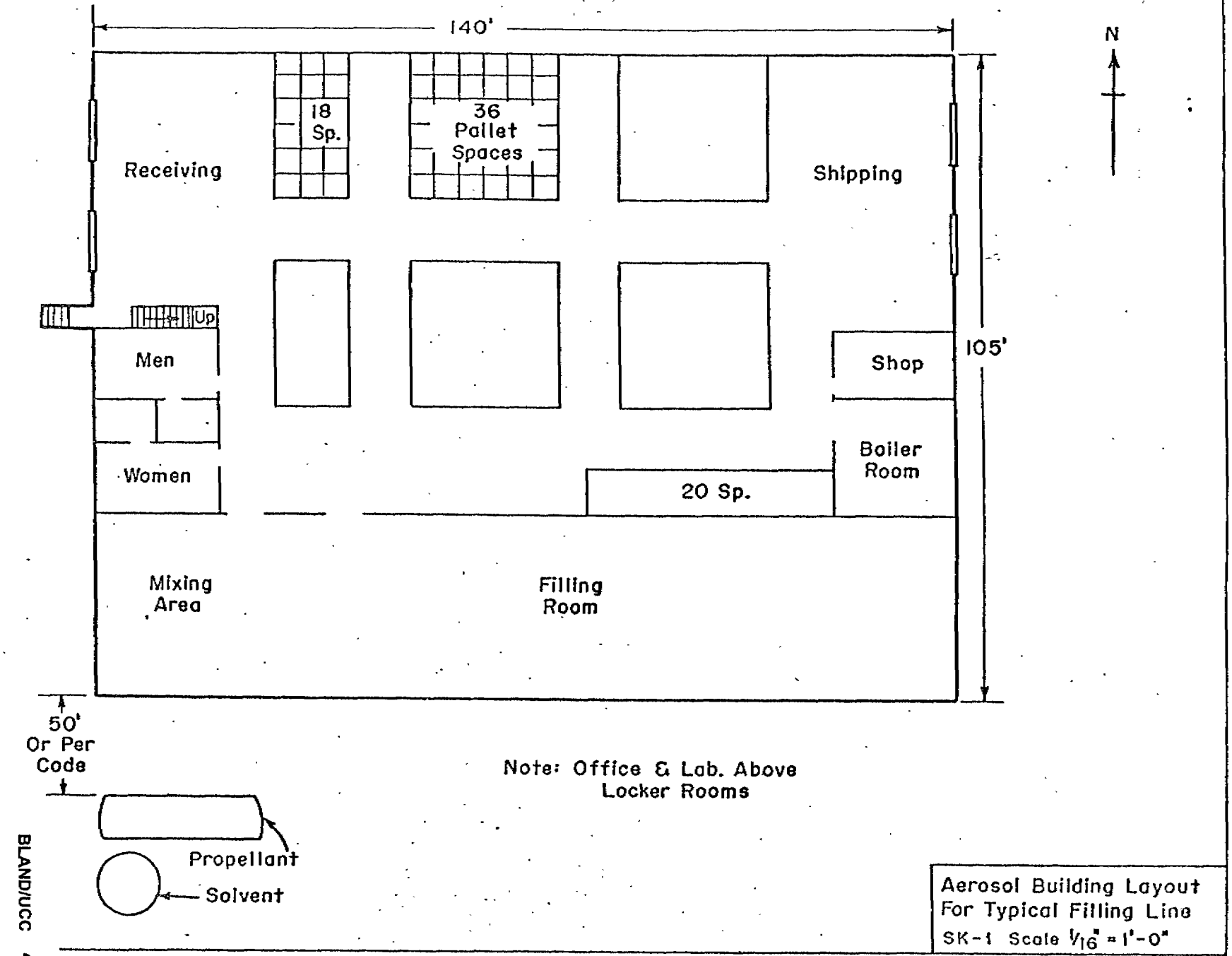


Figure 3.

In a building of this type, we suggest that the bays be as large as possible. In this particular situation, a span of 35 feet would be appropriate. Although longer spans such as this cost slightly more, owing to more complicated steel work, we believe the extra investment is well worth while. Eliminating columns permits more effective space utilization and gives greater flexibility in planning layouts.

Based on recent experience, we believe a suitable building can be erected for $8.00 per square foot. This is based on a reinforced concrete floor 3'-6" above grade and includes grading, lighting, ventilating, plumbing and sprinklers, but excludes site development and any landscaping. If topography and soil conditions permit placing the slab at grade level with truck docks depressed, a saving of about $0.50 per square foot should be possible. However, since the feasibility of placing the slab at grade depends on local conditions, we have based our estimate on the $8.00 figure.

The building thus far is heated, prime warehouse space. However, special areas such as the filling room, office, and quality control laboratory require additional features. In the case of the filling room, extra ventilation and lighting and a partition to separate it from the warehouse section are all that are necessary. This will provide operator comfort and will make it easier to maintain cleanliness. Tile walls or floors are not necessary in most installations of this type. On this basis, estimated filling room cost is $9.50 per square foot, a premium of $1.50 per square foot over the basic building cost.

On a similar basis, the locker room, lunch room, and shop should cost $12 per square foot. The laboratory and office are estimated at $16 per square foot.

Based on these unit costs, estimated total cost of the building shown in Figure 3 is $135,000. No allowance has been made for paving, since the type and extent of paving required depend on the specific site. However, these costs can easily be added as required.

BULK STORAGE

As shown in Figure 3, we recommend two tanks for bulk storage of the major raw materials. These tanks are shown 50 feet from the building, but this distance may be varied to suit local building code requirements for storage of red label products. The tank farm is designed for truck receipt, and separate tanks are included for alcohol and propellant. All tanks and transfer piping can be made of steel. Transfer piping to the building can be on a simple pole-type pipe rack, and a dike should be provided around the alcohol tank.

At peak levels of production, alcohol usage would be about 1,900 gallons per day. To meet this demand we recommend a 10,000-gallon vertical, dished-head tank. This tank could readily receive 6,000-gallon truckloads. Occasional receipts of 8,000-gallon loads, which can be made in certain areas without exceeding highway weight limits, could be handled. The tank would be 10'-6" in diameter and 18'10" in height and should include a level gauge and thermometer at the tank. Including a 100-gpm transfer pump with mechanical seal and unloading and transfer piping, we estimate the installed cost a $8,000. If tank car receipts are anticipated, the tank size should be increased to at least 15,000 gallons. The additional

capacity would be relatively economical; the tank cost would increase by about $1,500.

To handle the peak propellant demand of 1,800 gallons per day, we would suggest a 7,500-gallon horizontal, standard propane tank. Although a normal delivery would be 3,000 gallons, a smaller tank (holding, say, 5,000 gallons) would be too restrictive. The proposed tank would be 84" in diameter and 27' long with a 10-gpm pump to feed the production line. Such a unit with necessary auxiliaries is estimated at $9,300 installed.

Should a filler require a flexible plant capable of filling many different products, additional tankage would be necessary. In the normal case, we would recommend duplicates of the alcohol and propellant tanks described above. A duplicate of the alcohol tank would be suitable for most of the common solvents, and the propellant tank, which is rated at 250 psig, could be used for any of the liquefied gas propellants in commercial use today. In a flexible installation, at least one additional propellant tank would be necessary. This would permit the filler to custom-blend UCON propellants in any desired proportions. If desired, a filler could start with the two basic tanks described above, adding additional tankage as product variety increases.

We suggest that tanks be generously sized for flexibility, and because savings from reducing tank size are relatively small. For example, if the alcohol tank were cut to 6,000 gallons, the investment would be only about $1,000 less. Further details on tank farm design and specific recommendations to meet a filler's individual needs are available on request from the Olefins Division of Union Carbide Corporation.

MIXING

The peak concentrate requirement will be about 2,100 gallons per day. To handle this volume, we suggest two vertical, dished-head tanks with a nominal capacity of 2,400 gallons for mixing the main components. These tanks would be 6'-6" in diameter by 12' high, and we would suggest 304 stainless steel for the mix tanks and transfer piping to the filler.

In operation, each tank would hold a one-day supply of concentrate, and mixing could be done in one tank while the other tank was feeding the line. As alcohol formulations are usually easy to mix, we would suggest a pump rather than an agitator for mixing, since a pump should be effective as well as economical. Two pumps should be provided: one with a minimum capacity of 100 gpm for mixing and one with a capacity of 25 gpm for feeding the line. Both tanks should be piped to both pumps and the feed pump should recycle a portion of the concentrate through the tank to maintain a well-mixed blend.

For measuring the alcohol component, we suggest a meter system such as the A. O. Smith T-10-T. Properly maintained meters are more accurate and less expensive than weigh tanks. One meter should be installed in the transfer line from the tank farm as close as possible to the mix tanks. For alcohols, we suggest meters with no brass or aluminum parts and with automatic temperature-correction and an automatic cut-off valve. The temperature-correction will adjust for a 100°F. temperature spread, and the cut-off valve will automatically stop the flow when the pre-set volume has passed through the meter. A 2" meter system good for 20 to 80 gpm would cost $650 plus installation. A 1½" system good for 12 to 48 gpm would cost about the same. The installation cost of the two 2,400-gallon

tanks with transfer piping and meters is estimated at $18,500.

To handle minor components such as fragrances, surfactants, and the like, we would suggest a 460-gallon stainless steel tank, 4' in diameter and 6'-6" high. Drummed and bagged materials could easily be added to such a tank and premixed with a portion of the solvent. To facilitate mixing, this tank could discharge to the suction side of the 100-gpm mixing pump previously mentioned. We estimate the installed cost of this small tank, including a transfer pump and piping, at $5,600.

Our recommendation of metered tanks with mixing by pump is based on one easy-to-mix formulation (with minor variations possible). If many bulk liquids must be handled, each would require its own meter system for accuracy. Each meter would cost about $900 installed; with a large number of products, a weigh tank might be more feasible. A weigh tank would give complete mixing flexibility, but each filler must determine whether the added cost is justified. Similarly, using a pump to mix the concentrate would not be suitable with some difficult-to-mix materials. Should agitators be required, the installed cost of each 2,400-gallon mix tank would increase by about $4,000.

FILLING LINE

A typical working day on a packaging line is 450 minutes long, owing to personal time and time lost in starting up and shutting down. In addition, provision must be made for minor breakdowns on the line, lack of material and similar delays. To allow for this, we have based capacity on 420 minutes per day actual operating time. To fill the required 50,000-units/day, the line speed must average 119 units per minute. Since 120

per minute is a common break point in aerosol line speeds, we suggest a line which can be rated at this speed after a break-in period estimated at two to three months.

The speed rating of 120 units per minute has become almost a standard in aerosol design over the years. However, recent technological improvements have virtually made this break point obsolete as a limiting factor. Equipment is now available for line speeds of double this figure, and almost any intermediate rating can be handled. Selection of the rated speed is one of the key decisions a filler must make in preparing design criteria for a filling line. Although the line described here will fill 120 cans per minute (since this is adequate for the assumed annual demand), it could easily be upgraded by using larger equipment of the same general type.

There are three basic methods of filling aerosol cans with propellant, as mentioned before (cold filling, pressure filling, and under-the-cap filling). Many products use small valves (body size of .016" to .018"), which are not suitable for pressure filling since propellant flow through such a narrow orifice would be uneconomically slow. However, an acceptable alternative in most cases would be to use a valve with a large (.080") pressure-fill body orifice while keeping the small orifice for product discharge. Such a valve could be pressure filled at a rate of about 90 grams per second, thus permitting pressure filling at high speeds. It normally should have no effect on formulation, spray pattern or valve cost. For purposes of this report, we have assumed that valve and product specifications will permit any of the three filling methods to be used.

Although cold filling was the original aerosol method, we do not recommend it for the following reasons:

1. Refrigeration equipment is expensive.
2. Many of the available cold fillers have a maximum speed of 120 per minute, precluding any upgrading of the line.
3. Propellant losses can be sizeable.
4. Chilling to -30°F. for filling followed by heating to +130°F. for testing is not economical.

Under-the-cap filling and pressure filling both offer significant advantages over cold filling. Although under-the-cap filling equipment costs about 5% more than a comparable crimper and gasser, less floor space is required and set-up time is reduced by having only one machine. Performance of both under-the-cap and pressure filling equipment is improving rapidly and both should be considered by any packager planning a new filling line. The choice between the two is a close one and normally will depend on local conditions and the products to be handled.

For our purpose a pressure filling installation is assumed. It will provide ample capacity without pushing key components of the line. In the following sections, each major item of equipment will be discussed in detail. Although we suggest specific items, in most cases there are perfectly acceptable alternates which might be preferable for reasons of standardization or personal experience. A list of some leading equipment suppliers is included in Appendix "O" to serve as a guide in this area. More complete listings can be found in trade directories and buyer's guides. Most major items of equipment either have excess capacity or can be readily enlarged.

This flexibility costs very little and provides a high degree of insurance against being outgrown.

A typical layout of the proposed line is shown in Figure 4. The unscrambler and case-sealer have been placed outside the filling room to minimize lift truck traffic in and out of the main filling area. In addition, we recommend that all electrical equipment in the filling room be explosion-proof, in view of the potential hazard in handling volatile, low-flash solvents. In selecting equipment for the line, we have concentrated on continuous-motion rather than intermittent-motion machines, since aerosol cans tend to be unstable. Although an intermittent-motion, straight-line package installation might be available at slightly lower cost, such lines tend to require more adjustment and maintenance work, and they are not adaptable to convenient upgrading. In addition, they do not give the flexibility of a line in which each component has been picked to meet the individual needs of the filler. Also, except for contact parts in the fillers and the water bath tank, we believe carbon steel is an acceptable material of construction.

(Figure 4)

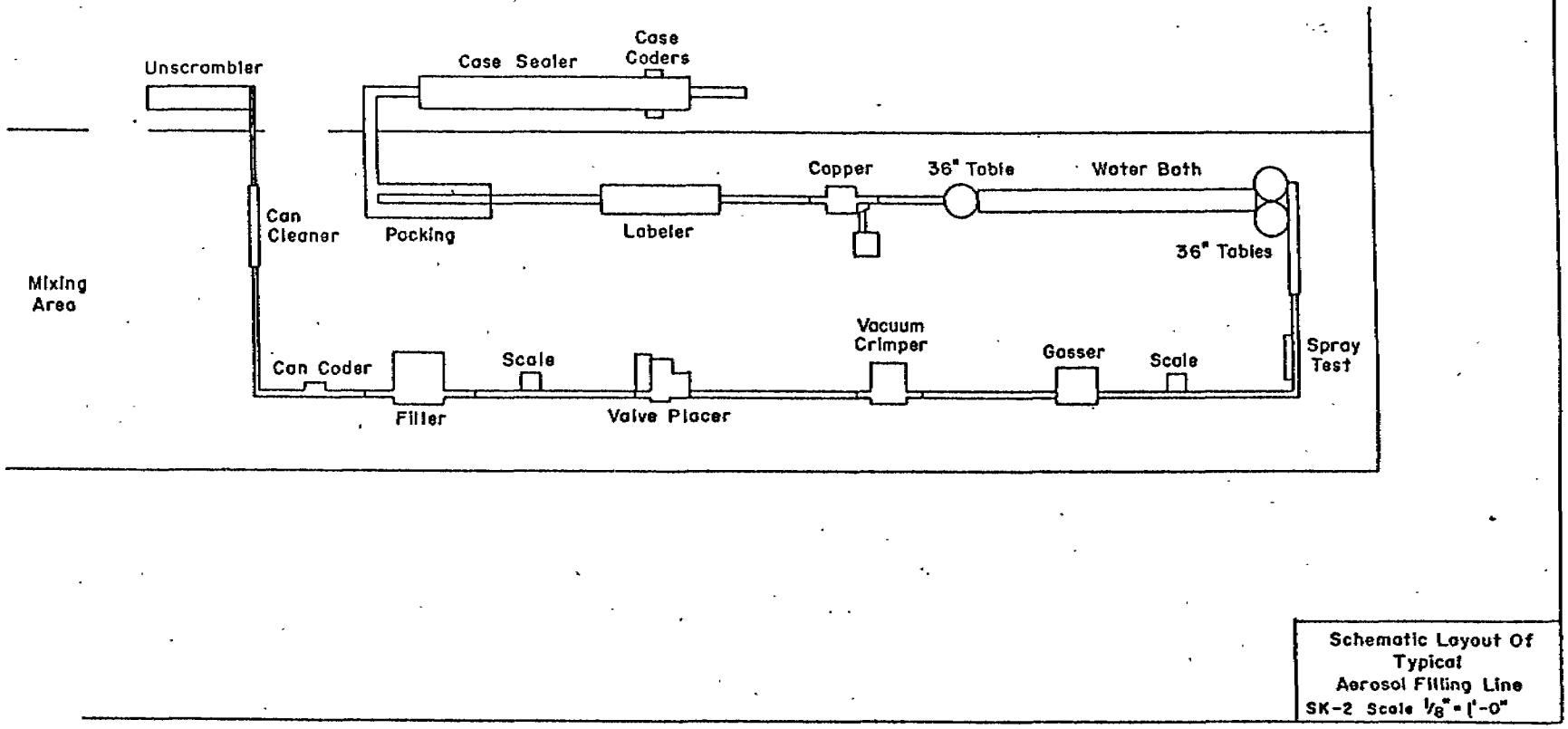


Figure 4.

Unscrambler

The first major item of equipment is an unscrambling table. The layout is based on receiving empty cans in bulk. If occasional use of reshipper cartons is made, a portable conveyor can be used to transfer the empty cartons to the packing area. A suitable unscrambler would be the Styl-O-Matic straight line unscrambling table without hood, made by Island Equipment Corporation of Miami, Florida. This unit handles the cans on steel table-top chains (3 chains, each 7½" wide) and discharges to an adjacent 4½"-wide chain conveyor. It will handle up to 240 cans per minute, depending on container size and the method of loading the unscrambler with empty containers. The purchase cost of a 9-foot-long unit made of carbon steel would be about $2,900.

Can Cleaner

To remove dust and stray fibers from empty cans, we recommend a jar-inverting and cleaning line such as that made by the Chisholm-Ryder Company, Hanover, Pennsylvania. This unit inverts, air-cleans, and re-inverts each container. It should handle 150 to 160 per minute, and we estimate the cost in explosion-proof construction at $1,800. Change parts (twisters for different-size cans) should cost about $125 per set.

Concentrate Filler

There are a large number of liquid fillers available which can handle the production rate required for the filling line being considered. Required capacity depends partly on container size and partly on the percent of container capacity that must be filled. We suggest a rotary, continuous-action machine to maintain positive container control. One suitable machine is made by MRM Company of Plainview, New York. This machine is a vacuum

filler with all contact parts of stainless steel. A 16-stem machine rated at 130 pint containers per minute should be ample. The estimated purchase price of such a unit, including centering devices and explosion-proof motors, is $6,900. Change parts for different size cans should cost about $250 per set.

Valve Inserter

Automatic valve inserting is a relatively new development. However, there are several machines available which can handle 120 containers per minute. Since two to three workers would be needed to insert valves manually at this rate, automatic insertion is definitely worth while. The RVP-4000 Valve Placer made by PMC Industries, Hackensack, New Jersey, should be suitable. This machine is rated at 140 units per minte. Valves are dumped at random into a hopper that orients and inserts the valves automatically. The hopper will hold 600 to 1,000 valves. The cost of this machine is estimated at $11,600, including explosion-proof construction. An auxiliary valve-positioner to seat valves accurately is available at $1,000.

The RVP-4000 Valve Placer will handle valves with the actuator button attached. We would normally recommend purchasing valves with the button, to eliminate the button-placing operation after the gasser. However, should it be desired to apply the button after filling, we suggest a Liberty Spray-Tip Applicator made by Haumiller Engineering Company, Elgin, Illinois. This machine orients buttons from a feed hopper and will seat up to 160 per minute. Including change parts and explosion-proof design, the estimated purchase cost of this unit is $4,900. Additional change parts would cost $150 per set.

Crimper

A good machine for crimping valve assemblies is the Model 4 H.V.C. made by John R. Nalbach Engineering Company, Inc., of Chicago, Illinois. This is a fully automatic rotary unit which draws a 20" vacuum to remove air from the can before crimping. It will operate at speeds up to 120 cans per minute. Including one set of change parts and explosion-proof construction, the estimated cost of this machine is $16,000. Should production demands increase, this unit could be converted in the field to an 8-head machine with twice the capacity, and at a nominal cost.

Gasser

The key piece of equipment in any aerosol line is the gasser. To charge the containers with Ucon propellant, we can recommend the Model 3-9 Gas Jet Aerosol Charger made by Karl Kiefer Division of Cherry-Burrell Corporation with the 290-cc cylinder on each charging stem. This cylinder will handle the 11-ounce container with a single stroke. Should it be necessary to charge more than 290 cc of propellant per can, a simple adjustment will permit two strokes per can for a maximum charge of 580 cc. This would, of course, reduce the machine speed by up to 50%. This machine has 9 stations and has a maximum speed of 250 units per minute at a charging time of one second. However, speed calculations are based on a maximum of 120 per minute. At a charging rate of 90 gms per second, the 11-ounce container will require 2.7 seconds to charge. With this charging time, the gasser is rated at 129 per minute. The machine is rated at 120 cans per minute at a charging time of 2.85 seconds.

At the rates specified above, the gasser could be a limiting factor, since it will take 248 days to produce the annual volume specified in the design basis. However, the calculated charging times are conservative, and in actual practice the Model 3-9 might perform noticeably better. This is supported by the current trend to faster-charging valves. Actual charging tests are suggested before the gasser is finally sized.

The recommended charger, including slack fill detector, can-ejector and over-the-button gassing attachments, can be purchased for about $19,000. Like the crimper, this machine can be modified in the field to handle increased production. In this case, the conversion would be to a Model 3-18, an 18-head machine which has a maximum mechanical speed of 300 units per minute but whose practical capacity is double that of the Model 3-9 at charging times in excess of 2 seconds.

As noted above, the Model 3-9 gasser has only 2 days extra capacity per year with the limiting speed of 120 per minute imposed by the crimper. Should a greater degree of flexibility be desired, a Model 3-12 charger could be purchased for about $3,000 additional. However, field conversion of a 12-head to an 18-head machine is not as simple as from a 9-head unit. Therefore, careful determination of design speed and flexibility requirements is essential to ensure that the proper size gasser is selected.

As part of the discussion of gasser capacity, it should be noted that charging time can be decreased (and speed increased) by adding part of the UCON-11 at the concentrate filler. However, this would require at least one additional propellant storage tank. In the current situation, the added investment in tankage would more than offset the reduction in cost of the gasser.

Water Bath

A Styl-O-Matic heat-and-leak test tank made by Island Equipment Corporation can be used to satisfy I.C.C. testing requirements. Based on an ambient temperature of 70°F., an 18-foot long tank is needed. To handle 120 units per minute, cans should move in four lanes. With a conveyor speed of 10 feet per minute, cans would be on 4" centers. The estimated cost of a stainless steel tank with two 7-1/2"-wide stainless steel conveyors, heating coils and controls, and a locally fabricated safety hood, is $10,800. This figure includes a simple air jet system at the discharge end of the tank to remove water from the valve cups. Rotary tables at each end of the tank to divert one lane of cans into four at the entrance and four into one at the exit are covered under "Conveyors." A four-lane, hold-down system costing about $11,300 installed would be required to handle non-magnetic containers (such as glass).

Overcapper

To apply the standard 1-3/8" plastic dust cover to filled cans, we recommend the Model FAB Fully Automatic Fitment Applicator made by Resina Automatic Machinery Company, Inc., of Brooklyn, New York. This unit is rated at up to 200 per minute. Since the standard machine operates with gripper chains, no change parts are needed. An explosion-proof model will cost about $4,100.

The standard machine hopper will hold about 7,000 caps. However, this hopper is about 6 feet above the floor and is difficult to service. To insure smooth operation, we recommend an attached escalator hopper at $1,500 as an accessory.

The Resina capper cannot handle full-body caps. The Pneumatic Scale Corporation's Automatic Can Lidder with 3A Sterling cap feeder will handle caps up to 89 mm in diameter. Including an elevator hopper, it should cost $9,800.

Labeler

A minimum-cost machine for applying wrap-around labels to the cans is the Chisholm-Ryder Model V4 New Way Labeler. This machine is rated at 350 per minute in the 211 size can. Including continuous feed attachment, twisters and other necessary accessories, the estimated puchase price of this machine is $4,400. In installing this machine, the feed conveyor must be slightly elevated (to 44") to avoid the use of a can elevator. Aside from the added cost, an elevator would limit the machine speed to about 140 cans per minute, but the 44" elevation should present no problem.

Case Packing

Since deal and combination packs are common in the aerosol industry, and since these require frequent changes in case sizes and packing patterns, the value of an automatic case packer is questionable. Allowance must be made for a packing table, however. Should a case packer be desired, a good unit is made by the Miller Hydro Company, Bainbridge, Georgia, and sells for about $15,000 including change parts. If the case packer is considered, it must be remembered that dimensions of corrugated cartons must be very closely controlled.

Case Sealer

To seal filled shipping cases and deliver them to a manual palletizing station, we can recommend a Model 52-22 fully automatic case sealer made by

Elliott Manufacturing Company of Fresno, California. This unit is rated at 700 cases per hour and uses a pressure glue system with ball-point-type applicators. Although the theoretical requirement is for only 600 cases per hour, a slightly larger machine would provide considerable flexibility for an extra cost of only about $150. A machine to seal both top and bottom flaps will cost about $4,900. If only the top flaps are to be sealed, $500 can be deducted from this price.

Coders

Equipment required for coding cans and cases depends on the information required and where it must be printed. For this report, it has been assumed that cans must be imprinted with a lot code on the bottom. To accomplish this, we can recommend a Sideline "Markocoder," Model SLM-2, made by Adolph Gottscho, Inc., Hillside, New Jersey. This is an extremely simple unit which fits over a section of conveyor. It operates from line pressure and is rated at 150 units per minute. It will print one line with a maximum of nine characters parallel to the direction of container movement. Including an ample supply of type, this coder will cost about $600. Additional sets of change parts would cost about $100 each.

Coding both sides of each corrugated carton is advisable, as this guarantees that the code can be seen on any pallet load stacked with an interlocking pattern. To do this, two Gottscho Model 602 coders are suggested. These units can be installed at the case sealer and will print a legend up to 8" long. They will repeat the legend every 9". Including type, the two case coders will cost about $300. Should coding requirements be too elaborate for the units described above, suitable coders could easily be provided at higher cost.

Conveyors

The actual conveyor requirement will depend on the final layout of the filling line. For handling cans, a 4-1/2"-wide chain-type conveyor made of steel, such as Island Equipment's Styl-O-Matic Can Conveyor, is recommended. This type of conveyor is fully compatible with all equipment in the filling line. If glass containers are to be handled, non-metallic chains and guides would be desirable.

Between the spray test hood and the rotary tables at the entrance to the water bath, the chain conveyor width should be increased to 7-1/2" to permit diverting the single line of cans into a double line. Each line of cans should feed one 36" table. The tables, in turn, will form four rows of cans for the test bath. At the end of the test bath, another 36" rotary table should be used to re-form a single row of cans on a 4-1/2"-wide conveyor for further operations.

A skate-wheel-and-belt conveyor system should be used to move filled cases from the packing table to the case sealer. A short length of belt conveyor should be at the end of the case sealer to facilitate the work of manual palletizing. A portable conveyor system can be provided between the unscrambler and the packing table should it be desired to use reshipper cases. A conveyor system such as described above, including can conveyors, rotary tables, and conveyors for cases, is estimated at $15,000.

In-Line Quality Control

In the proposed filling line, there should be three quality control stations. After the filler and after the gasser, "over-and-under" scales should be installed to checkweigh containers at random. After the second checkweigh station, a locally fabricated sheet metal spray test booth

with an exhaust duct should be installed for spot testing valve action. These three quality control stations can be installed for about $1,000.

If a flammable hydrocarbon propellant such as Ucon isobutane is to be used, all valves should be tested before the water bath to remove propellant from the dip tubes. The original spray test booth could easily be modified to handle this. With flammable propellants, the gasser and the spray test booth should be walled off from the remainder of the line, and a leak detector installed to minimize the hazard. Since the layout in Figure 4 has this portion of the line in the southeast corner of the building, necessary modifications can be made at low cost.

Installation Cost

All prices to this point have been purchase prices of the equipment with necessary accessories included. To install this equipment in accordance with the layout in Figure 4, the cost would be $15,000. This figure includes the power supply to the drive motors,which, for this layout, would total approximately 15 horsepower.

WAREHOUSING

The warehousing facilities shown in Figure 3 will provide a net usable storage area of 3,200 square feet, not counting the aisles shown in the sketch. In addition, a receiving area is provided on the west side and a shipping area on the east with two truck doors at each end. Estimated normal daily shipments and receipts is two to three truck loads each. However, to allow for LTL shipments and receipts and to avoid bottlenecks, four truck spots are recommended.

Of the total net usable storage area, 800 square feet should suffice for raw material storage. These materials would normally be stored one and two pallets deep from the aisles. This space should be ample for a two-day supply of cans, a one-week supply of caps, valves, and knocked down shipping cases, and a one-month supply of labels, chemical additives, and miscellaneous items. The space allowed for raw material inventory, particularly of empty cans, is minimal. However, a filling line of this size using standard aerosol cans should be able to schedule can delivereies closely. The buffer stock of cans would be to protect against an occasional missed delivery or emergency change in production schedule.

The layout provides 2,400 net square feet for finished good storage with materials stored up to three pallets deep from the aisles. Based on a maximum stacking height of 12 feet, this area should hold a maximum of 640,000 cans. However, the effective capacity is only 90% of this, or 580,000 cans. If more than 90% of the total space is used for storage, excessive re-handling normally results. A finished-product storage area of this size should be ample for twelve days' output, and should provide sufficient inventory for an orderly production schedule.

AUXILIARIES

An appreciable amount of auxiliary equipment must be installed in the areas indicated in Figure 3. A boiler and air compressor should be installed in the boiler room at the east end of the building. A 100-horsepower, 60-psi gas-fired package boiler should cost $5,500 installed and should be adequate for building heat and process steam. A 75-horsepower air compressor for plant and process air would cost about $10,000 installed. This is a relatively large compressor, but the gasser requires a great deal of air in its operation.

One lift truck would be adequate for warehouse handling. A 3,000-pound electirc truck with battery and charger would cost about $7,000. Electric power is recommended, since the service would probably be very intermittent. The truck chosen should be a narrow-aisle type. Although trucks are available that will operate in aisles less than 8 feet in width, the aisles in the preliminary layout are 10 feet wide to give flexibility. In addition, two hand pallet trucks should be provided, at a cost of $800.

The laboratory shown on the layout is intended for quality control, not product development. Basic tests on raw materials (such as color, odor, specific gravity, and refractive index) could be made here. Likewise, finished cans could be tested for moisture, specific gravity, pressure, and effectiveness of crimp. Basic equipment and shelving for retained samples would cost about $3,000. This does not include a chromatograph. A chromatograph with recorder would cost an additional $2,500 to $3,000.

Shop equipment including a drill press, hand tools, work bench, and shelving would cost about $1,500. Lockers, lunch room equipment and office equipment would also cost about $1,500.

LABOR REQUIREMENTS

Total labor requirements depend partially on layout and partially on company policy. Unless policy prohibits, most jobs on aerosol production lines are handled by women. Including indirect labor, the total estimated manpower is as follows:

1 man - Unload empty cans at the unscrambler.

1 girl - Checkweigh after concentrate filler.

1 girl - Checkweigh after gasser.

1 girl - At spray test booth

(Note: The three girls assigned to quality control work can also service the line in their respective areas since only a partial inspection is necessary.)

1 girl - Inspect for leaking cans at test bath.

1 man - Service the valve-placer and the capper.

1 man - Service the labeler and do general line-tending.

3 girls - At the packing table.

1 man - Palletize at the end of the case-sealer.

1 man - Provide empty cans to the unscrambler and remove pallet loads of finished product.

1 man - Receiving and shipping.

(Note: This assumes that most shipments are in truck-load lots and that carton addressing, picking small orders, and the like do not consume a significant amount of time.)

1 man - Day mechanic

1 man - Laboratory technician.

1 girl - Clerk.

1 man - Mixing operator.

1 man - Night mechanic and set-up man.

1 man - Supervisor.

The total labor requirement listed above includes 8 girls and 11 men. Set-up labor can be based on a rule of thumb of one man-hour per major item of equipment. For the line proposed, about 8 man-hours would be required for a complete set-up. This should be done at night to minimize line down-time. A partial set-up (one in which can diameter is not changed) would require less time. Although set-up time would not be a problem with only the 11-ounce can specified in the design basis, the limitation was made to simplify discussion of the filling line. In practice, multiple can sizes would be handled, and set-up labor must be allowed. If safety requirements call for a minimum of 2 men in a building, mixing could be done at night. In this case, the mixing operator would have to be capable of analyzing a blend to avoid lost time in the morning.

SUMMARY

The preceding sections outline a suggested approach to an aerosol filling line. We believe the approach is a workable one, but testing would be required before final sizing of equipment. As summarized in Table VII, the total installed cost (before engineering and contingencies) is estimated at just under $325,000. This is for the basic equipment; optional extras are not included.

To estimate the cost of a higher-speed line, a rough approximation can be obtained from the well-known "six-tenths rule." This is a rough rule of thumb that is reasonably applicable to a complete packaging line of this type. The rule can be expressed by the formula:

$$C_2 = C_1 \left(\frac{R_2}{R_1} \right)^{0.6}$$

where C_1 is the known cost of a filling line with capacity R_1,

R_2 is the capacity of the second filling line,

and C_2 is the unknown cost of the second line.

Although the hypothetical situation used as a design basis for this report will rarely occur exactly as set forth, the information given above should provide a useful frame of reference in approaching the design of an aerosol filling line. The basic filling line is quite flexible, being suitable for a wide range of container sizes; line speed can easily increased if necessary. Further assistance and more detailed information is available on request from the Olefins Division of Union Carbide Corporation.

VII. STORAGE AND HANDLING

This section presents detailed information concerning storage facilities for UCON® fluorocarbons. The flow diagram (Figure 5) shows the storage tank and recommended accessory equipment. Engineering details are provided in the Section titled "Equipment Specification Sheets."

UCON fluorocarbon bulk deliveries are made by tank truck or tank car. Tank trucks are equipped with an unloading pump and hoses. Unloading hoses are discussed here, but they need not be purchased by the customer if the truck can be driven to within about twenty feet of the unloading line connection. In the case of tank car deliveries, an unloading compressor must be provided, and an unloading station is needed so that operators can have ready access to the tank car dome.

Air should be evacuated from new storage tanks prior to filling them with fluorocarbon. For locations where general plant vacuum pumps are not available for evacuating storage tank and piping facilities on initial start-up, specifications are included covering both mechanical and steam-jet-type vacuum equipment that may be considered. This equipment can be brought in on a temporary basis during initial start-up or installed as permanent stand-by facilities required when system repairs are called for. It may also be feasible to rent a suitable vacuum pump from a refrigeration supply house.

Figure 5.

NOTES:

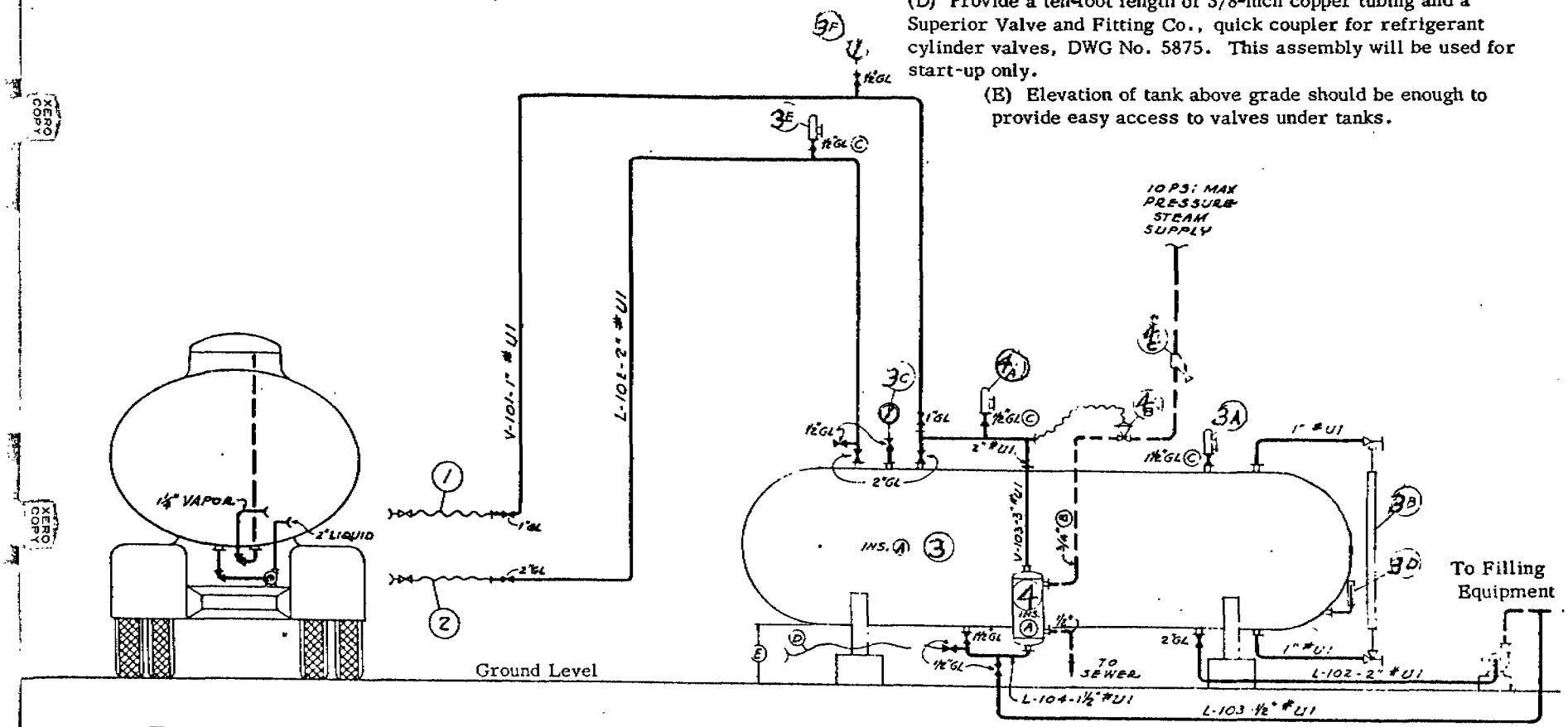
(A) Storage tank vaporizer, vapor lines and steam lines are to be insulated with one-inch thickness of 85% magnesia or equal. Tanks should be painted white after insulation to reduce heat absorption in the summer.

(B) Steam lines are to be installed in accordance with customer practice.

(C) Shut-off valves under safety valves are to be locked in the open position with a car seal or similar device.

(D) Provide a ten-foot length of 3/8-inch copper tubing and a Superior Valve and Fitting Co., quick coupler for refrigerant cylinder valves, DWG No. 5875. This assembly will be used for start-up only.

(E) Elevation of tank above grade should be enough to provide easy access to valves under tanks.



ONE-TANK STORAGE SYSTEM FLOW DIAGRAM

EQUIPMENT SPECIFICATIONS

1 - Unloading Hose Assembly

To connect to the tank truck and to equalize the pressure between the vapor space in the storage tank and the tank truck.

The assembly will consist of the following:

(a) One, 1-1/4-in. brass Evertite coupler, Part B, female end with male NPT threads, and Teflon gasket. Purchase with dust plug attached to coupling with a 6-in. length of brass chain.

(b) One, 1-1/4-in. x 1-in. bell reducer.

(c) One, 1-in. diameter nipple, 4 in. long.

(d) One, 1-in. Henry Catalog No. 2001 ductile iron globe valve with Teflon packing and gaskets.

(e) One, 1/2-in. steel globe valve, Henry Catalog No. 453, or equal.

(f) One, 15-ft. length of 1-in. corrugated metal hose, bronze with bronze wire braid cover. End connections are to be 1-in. NPT pipe nipples welded or brazed to each end of the hose. The hose must be suitable for pressure from full vacuum to 325 psig.

Assemble the unit with the coupling and the valve at the same end. Install the 1/2-in. globe valve between the union and the shutoff valve to relieve pressure before disconnecting the assembly. All threaded joints are to be made using Teflon tape as the thread dope.

2 - Unloading Hose Assembly

To connect to the unloading pump on the tank truck.

This assembly will consist of the following:

(a) One, 2-in. brass Evertite coupler, Part B, female end with male NPT threads, and Teflon gasket. Purchase with dust plug attached to the coupling by a 6-in. length of brass chain.

(b) One, 2-in. Henry Catalog No. 2301 ductible iron globe valve, with Teflon gaskets and packing.

(c) One, 1/2-in. steel globe valve, Henry Catalog No. 453, or equal.

(d) One, 15-ft. length of 2-in. corrugated metal hose, bronze with bronze wire braid cover. End connections are to be 2-in. NPT pipe nipples welded or brazed to each end of the hose. The assembly must be suitable for pressures from full vacuum to 325 psig.

Assemble the unit with the valve and the coupling at the same end. Install the ½-in. globe valve between the union and the shutoff valve to relieve pressure before disconnecting the assembly. All threaded joints are to be made using Teflon tape as the thread dope.

3 - Storage Tank No. 1

To store UCON fluorocarbons

Type:	Horizontal Pressure Vessel
Nominal capacity:	Per purchaser's recommendation
Nominal diameter and length:	Per fabricator's or purchaser's recommendation
Drawings:	To be supplied by the fabricator
Operating pressure:	Full vac to 200 psig
Operating temperature:	Ambient
Set pressure of relief device:	200 psi
Design pressure and temperature:	200 psi at 135°F.
Location:	Outside
Earthquake loadings:	Not required
Materials:	Steel
Corrosion allowance:	None
Erosion or abrasion allowance:	None
Design and construction:	Welded in accordance with ASME Code and attached specifications
ASME Code Inspection & Code stamp:	Required
Hydrostatic test:	1½ times max allowable pressure
Pneumatic test:	250 psi
Stress-relief:	If required by ASME Code
Radiography:	If required by ASME Code
Leak test: (Halogen)	Required

Connections,	
Liquid inlet:	One, 2-in., top
Liquid outlet:	One, 2-in., bottom
Spares:	One, 2-in., top; One, 1½-in., bottom
Pressure gauge:	One, 1-in., top
Gauge column	One, 1-in., top; One 1-in., bottom
Thermometer:	One, 1-in. coupling head, lower half
Safety valve:	One, 1½-in., top*
Flanges:	300-lb ASA
Manhole:	As required by ASME Code
Baffles:	Not required
Grounding clips:	Not required
Gauge-column clips:	Required
Ladder clips:	Not required
Vessel support:	Provide support saddles

Notes: 1. Tanks located in areas where flammable materials are stored will require safety valve connections larger than 1½ in.

2. Filling liquid will have a specific gravity of 1.5.

3B - Liquid Level Gage Assembly

To provide visual indication of the liquid level in the storage tank.

Make:	Jerguson or equal
Type:	Armored reflex
Fig. no.:	620-R-5, visible length to equal or slightly exceed the diameter of the storage tank.
Material:	Steel
Connections:	1/2 in. screwed
Operating pressure:	Full vacuum to 200 psig
Operating temperature:	60°C maximum

Note: Two shutoff valves (Jerguson No. 66U-C) should be purchased with the gage. A support bracket, similar to Jerguson Drawing No. GD-961, should be mounted at the mid-section of the gage by the manufacturer.

3C - Pressure Gage

To indicate the pressure of the vapor above the liquid in the storage tank.

Make:	Ashcroft Duragage or equal
Movement:	All stainless steel, geared
Case:	1279, black phenol plastic
Dial:	4-1/2-in. diameter, white, black figures
Range*:	30-in. Hg vac to 30 psig
Bourdon tube:	Series A, phosphor bronze
Connection:	1/2-in. NPT, bottom

* For "Ucon" Fluorocarbon 11 only. For mixtures containing "Ucon" Fluorocarbon 12 or pure "Ucon" Fluorocarbon 12, specify a range of 30-in. Hg vac to 200 psig.

3D - Indicating Thermometer

To indicate the temperature of the liquid level in the storage tank.

Make:	Rochester 1748 or equal
Range:	25^{o} to $125^{o}F$.
Dial:	3 in. diameter, white, black figures
Stem length:	6 in.
Installation:	Install in a brass separable socket with 1-in. NPT threads for the tank connection, 1/2-in. NPT threads for the thermometer to permit removal of the thermometer without disturbing the tank contents.

3E - Relief Valve

To relieve pressure resulting from thermal expansion of the liquid in the liquid-inlet line to the storage tank.

Make:	Henry, Catalog No. 560-A, or equal
Size:	1/2 in. by 3/4 in.
Material, body:	Steel
nozzle:	Stainless steel
disc:	Stainless steel
spring:	Steel
Set pressure:	200 psig
Operating temperature:	Atm

3F - Pressure Gage

To indicated the pressure in the vapor equalizing between the tank car and the storage tank.

Duplicate Item 3C.

4 - Vaporizer No. 1*

To maintain positive pressure in the storage tanks and to prime the unloading pumps.

Performance Data

	Tube Side	Shell Side
Material entering, weight per cent,		
UCON® Fluorocarbons:	100%	
Atmospheric steam:		100%
Material evaporated, weight per cent,		
UCON Fluorocarbons:	100%	
Material leaving (vapor phase), weight per cent,		
UCON Fluorocarbons:	100%	
Total quantity, entering:	400 lb/hr max.	
evaporated:	400 lb/hr	
leaving:	400 lb/hr	

(Continued)

	Tube Side	Shell Side
High temperature:	41°C	
Condensing temperature:	41°C	
Low temperature:	0°C	
Estimated quantity of heat transferred,		
Total:		100,000 Btu/hr
Corroding tendency:	None	None
(for specified constr. materials)		
Fouling tendency:	None	None
Physical properties of single compound or the compositemixture,		
Temperature:	20°C	100°C
Molecular weight:	121 to 137	
Viscosity, liquid:	0.3 cp	
Specific gravity, liquid:	1.4 to 1.6	
Specific heat, liquid:	0.21 Btu/lb °F	
Density, vapor:	0.606 lb/cu ft	
Latent heat:	76 Btu/lb	
Surface tension	19 dynes/cm	
Operating pressure:	10 psi	Atm
Allowable pressure drop:	-	-
Mechanical design pressure:	200 psi	150 psi
Set pressure of safety valve:	200 psi	-

*Used for outside tanks containing UCON 11. Not needed for UCON 12 and high-pressure blends.

	Tube Side	Shell Side
Connections,		
Inlet:	1-1/2-in. screwed	3/4-in. screwed
Outlet:	3-in. silver-soldered or brazed	1/2-in. screwed
Type of unit:	Shell and tube, heat exchanger, vertical, with straight tubes, and fixed tube sheet	
Maximum permissible over-all length:	30 in.	
Minimum permissible tube diameter:	3/8 in.	
Materials, shell:	Copper	
heads:	Brass	
tubes:	Admiralty	
tube sheets:	Brass	
gasket material:	Teflon-filled Flexitallic	

Purchase a Ross HCF type heat exchanger, 16 sq. ft. of heat-transfer surface

4A - Safety Valve

To pretect the vaporizer from overpressure in the event that it is valve-closed while filled and the steam heat is left on.

Make:	Henry, Catalog No. 560-A, or equal
Size:	1/2 in. by 3/4 inc.

(continued)

Material, body:	Steel
nozzle:	Stainless Steel
disc:	Stainless Steel
spring:	Steel
Set pressure:	100 psig
Operating temperature:	Atm

4B - Temperature Regulator

To control the vapor pressure generated in the vaporizer by throttling the steam flow:

	Tube Side	Shell Side
Performance Data		
Material handled:	5-10 psi steam	
Quantity, norm:	75 lb/hr	
Molecular weight, vapor:	18	
Temperature:	121°C	
Pressure, upstream:	5-10 psig	
downstream:	Atm	
Line size and spec.:	3/4 in., steel	

Note: Temperature in vapor line from vaporizer should be 70° to 105°F. Manual adjustment of temperature setting is required.

Purchase Specifications

Manufacturer:	Leslie
Model No.:	ME-1-D, with temperature adjustment

(continued)

Body size:	1/2-in., screwed
Inner valve size:	3/8-in.
Rating:	200 psi
Operating range:	70-120°F
Material, body:	Bronze
trim:	Stainless Steel

Furnish with No. 3 stainless steel casing and 10 feet of flexible tubing.

4C - Strainer

To protect the steam throttling valve of the temperature regulator.

Make:	Sarco, or equal
Size:	3/4-in., screwed
Body:	125-lb., cast iron
Screen:	Bronze, monel or stainless steel
Perforations:	1/64 in. approximately

SPECIAL VALVE AND PIPING SPECIFICATIONS

GENERAL

Maximum Pressure: 200 psi

Temperature Range: Atmospheric

PIPING

Item		Size, incl.	Specification
Construction		To 3"	Screwed
Fabrication		To 3"	To equal or exceed requirements of the ASA Code for Pressure Piping (ASA B31.1), Section 6, Chapter 2.
Pipe	Material	To 1-1/2"	Steel, butt-welded: ASTM A53
		2" to 3"	Steel, electric-resistance-welded or seamless: ASTM A53 Grade A or B
	Thickness	To 3"	Schedule 40.
Elbows, Tees and Other Fittings -	Type	To 3"	Forged steel screwed: 2000 lb. (minimum) or ductile iron screwed: ASA 250 lb.
Flanges -	Type	To 3"	Forged steel or ductile iron, screwed: ASA 300 lb.
	Facing	To 3"	Manufacturer's standard

(continued)

Item		Size, incl.	Specification
Unions -	Type	To 3"	Forged steel screwed: 2000 lb. (minimum).
Pipe Plugs -	Type		Steel.
Bushings -	Type		Steel.
Gaskets -	Type	To 3"	Durabla or equal.
Dope -	Threads	To 3"	Teflon Tape: Permocel Ribbon Dope No. 412 thread sealant, or equal.
	Gaskets	To 3"	Shellac.
Flange Bolting -	Studs	-	Alloy steel: ASTM A193 Grade B7, B7A, or B14.
	Nuts	-	Alloy steel: ASTM A194 Grade 2 or 2H.

VALVES

Type	Size	Identification	Make and Figure Number	Body	Trim	Type of Ends
Globe	1/2"	GL	Henry 320	Semi-steel	Steel	Screwed
	3/4"	GL	Henry 330	Semi-steel	Steel	Screwed
	1"	GL	Henry 340	Semi-steel	Steel	Screwed
	1-1/2"	GL	Henry 220	Semi-steel	Steel	Screwed
	2"	GL	Henry 230	Semi-steel	Steel	Screwed
	2-1/2"	GL	Henry 240	Semi-steel	Steel	Screwed
Check	1/2"to2"	CK	Vogt 2501-8	FS	Steel	Screwed

CLEANING AND TESTING THE STORAGE SYSTEM

To prevent contamination of UCON Fluorocarbons with rust and foreign matter, all interior surfaces of the tanks and interconnecting piping should be dry, clean, and rust-free. This is best accomplished by grit blasting, done as the last phase of construction.

Leak testing should be done after the system has been assembled but before the final cleaning to reduce the sources of contamination to an absolute minimum. Leaking joints can be located by introducing a few pounds of UCON Fluorocarbon 12 into the system, raising the pressure to 150 to 200 psi with dry air, nitrogen, or carbon dioxide, and checking all joints with a halogen torch or a G. E. Type H-1 Leak Detector. Leak detectors can be rented or borrowed from a tank fabricator.

The joints using spiral-wound, Teflon-filled gaskets that must be opened for the cleaning operation should be fitted with asbestos gaskets for the test. Spiral-wound gaskets, particularly for manholes, are difficult to replace on short notice.

Before sandblasting, all tank nozzles not openend for this operation should be wire-brushed and plugged to keep grit out of the valves and fittings. Tight-fitting wooden plugs are recommended. The tank should be thoroughly vacuum-cleaned and evacuated immediately after sandblasting, since an overnight delay would allow some oxidation of the cleaned surfaces. Upon reassembly after cleaning, the system should be capable of holding a vacuum of 28 inches of mercury for eight hours with no appreciable rise in pressure; pressure rise would indicate either a leak or the presence of moisture in the system. If the system is not placed in service immediately after final

cleaning and testing, it should be pressured slightly with dry nitrogen. Air should not be admitted into the system after the final cleaning.

If a small amount of lubricating or refrigeration type oil can be tolerated in the UCON Fluorocarbons, the tank fabricator will, at a modest cost, grit-blast the interior of the vessel and apply an oil film to prevent oxidation.

Contamination from the interconnecting piping should not be objectionable.if only the straight pieces of pipe are sandblasted immediately before fabrication. All traces of cutting oil should be carefully removed from the pipe threads before sandblasting and fabrication.

This work can be done by firms that specialize in cleaning equipment of this type. Chemical cleaning is not recommended, since our experience with it has been unsatisfactory.

FILLING UCON® FLUOROCARBON STORAGE SYSTEMS FROM TANK TRUCKS

Since the tank trucks are fitted with gasoline-powered pumps, filling storage systems from them will be very simple. In most cases, it will be simply a matter of connecting the hoses and starting the truck-mounted pump. However, the following suggestions and comments should be considered:

(1) Before filling the system, it should be evacuated to a vacuum of 28.5 inches of mercury, or greater if possible, and held for eight hours. The system should then be filled as soon as possible to prevent leakage of air and moisture into the tank. If it cannot be filled immediately, the vacuum should be broken by introduction of just enough Fluorocarbon (from cylinders) to produce a slight positive pressure in the tank.

(2) If initial filling of the system can be started while it is under vacuum, connect only the liquid-unloading assembly and start the pump. Do not connect the vapor return line until the system is under positive pressure.

(3) Unloading hoses for handling very volatile mixtures of UCON Fluorocarbons should be fitted with a small valve near the quick coupling to relieve pressure before disconnecting the hoses.

(4) Carefully clean and dry the hose ends before making the connection.

(5) Do not start the unloading operation in rain or snow unless the unloading spot is sheltered.

(6) Any part of the system opened for repair should be thoroughly cleaned and either evacuated, or purged with the UCON Fluorocarbon it is to handle, before it is placed in operation.

(7) If it is necessary for workmen to enter the storage tank, either the tank should be force-ventilated or the workmen should be fitted with air masks. UCON Fluorocarbons are non-toxic, but oxygen is necessary to support life.

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GENERAL APPENDIX

Appendix A

DIMETHYL ETHER/FLUOROCARBON AEROSOL PROPELLANT BLEND

By

R. J. Scott And R. R. Terrill

Technical Service Laboratory

Union Carbide Corporation

Chemicals Division

Tarrytown, New York

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MANY liquefiable gases could, on the basis of vapor pressure alone, serve as aerosol propellants. When factors such as toxicity, safety, cost, and reactivity are considered, the number is narrowed to but a few. Of these, general acceptance has been accorded to fluorocarbons as fulfilling most of the requirements imposed by safety and utility.

Other potential liquefied gas propellants are flammable and require special equipment for handling and storage. For many years there has been an interest in combining these materials with the fluorocarbons in the hope that the resulting mixture would still be nonflammable. Reed (1) developed one such mixture, known as "Propellant A." It consists of 10% isobutane and 90% fluorocarbon 12/11 50/50.

The fact that one, useful, nonflammable mixture was defined suggested the probability that others could be determined. Therefore, some time ago the technical service laboratory of Union Carbide Chemicals set out to survey the whole field of aerosol propellants and propellant blends. Our objective was to determine the criteria for a safe, nonflammable blend and, then, devise blends that would meet these standards.

We soon found it necessary to separate the candidates according to the intended application. The reason for this is the difference in boiling points (and, hence, in pressures) and the opportunity for fractionation when two materials differing in boiling points are mixed together. Isobutane, for example, would not make a good blend with fluorocarbon 12, because it lowers the pressure and tends to separate, producing a flammable vapor. With fluorocarbon 12/11 50/50, however, the pressure is not significantly changed and the vapor coming off at the beginning and the end of a fractionation is at all times rich in fluorocarbon relative to the flammable constituent. In other words, there is what might be called a "head" and "tail" arrangement, with nonflammable fluorocarbon coming off before, with, and after the flammable component. Such an arrangement is necessary with all propellant blends involving flammable materials that have significant differences in boiling points.

Propellant A is a moderate pressure propellant. The question soon arose as to the possibilities of a high pressure blend for products now utilizing straight fluorocarbon 12, primarily aerosol paints. Dimethyl ether attracted our attention as a prime candidate for one of the components. It boils at −24 C., has a pressure of 60 psig. at 70 F., and a K-B value of 91, indicating good compatibility with paint resins.

The use of dimethyl ether as an aerosol propellant is not new, it was suggested by Rotheim as far back as 1931 (2). Vapor mixtures of dimethyl ether and fluorocarbon 12 have been investigated by the Bureau of Mines (3), and although it was indicated that a nonflammable system could be devised, the manner of doing so has not been revealed in the published literature. In general, dimethyl ether did not find much use as an aerosol propellant, primarily because it is flammable and was not commercially available.

When, however, dimethyl ether did become commercially available, a study was initiated to determine if an economically attractive, safe, nonflammable blend of dimethyl ether and fluorocarbon could be developed.

Flammability

At the outset, a criterion was established that any blend that was developed would have to be nonflammable in a true scientific sense, and would have to be safe for use without requiring an investment in detection equipment and alarm system. Our concern was primarily with factory operations, such as storage, warehousing and filling, rather than simply complying with legal regulations on an individual prospect or container basis. The standard regulatory tests, such as flame projection and drum tests, were inadequate

for our purposes because of their arbitrary nature.

To determine true flammability of gases and vapors one must turn to the Bureau of Mines, and the concept of explosive limits which it has developed (4). Basically, an explosive, or flammability, limit is that composition of a vapor mixture which is capable of propagating a flame. For any given mixture there are two limits, a lower and an upper. The former represents the point at which there is sufficient flammable material present to propagate a flame; the upper limit represents the point beyond which there is too much flammable material, or, conversely, not enough air or oxygen present to propagate a flame. Very often, it is observed that a cap of flame forms around the source of ignition in the presence of flammable vapors*, but the flame is extinguished when the source of ignition is removed. Such mixtures have not reached the explosive limit and should not be regarded as flammable, for it is flame propagation that is the key which makes a gas or vapor dangerous. The Bureau of Mines has published data on explosive limits for a great many materials (4) and they are often quoted in physical property and specification tables.

As an inert gas or flammability suppressant is added to a mixture of a flammable gas and air, the explosive limits are brought closer together until they meet. This is pictured graphically as a flammability curve. Such a curve has been determined for mixtures of dimethyl ether and fluorocarbon 12 by the Bureau of Mines and is shown in Figure 1**. The vertical axis represents concentrations of dimethyl ether vapor and the horizontal axis represents concentrations of fluorocarbon 12. Note that the points on the vertical axis are the explosive limits in air. Any point inside the curve represents a flammable mixture; any point outside the curve represents a nonflammable mixture.

*Frequently observed with drum tests
**Reprinted from Bureau of Mines Report of Investigations 4125

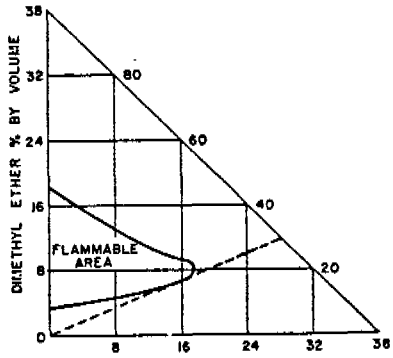

FIG 1: FLAMMABILITY CURVE FOR VAPOR MIXTURES OF DIMETHYL ETHER AND FLUOROCARBON 12

The chart is interpreted as follows: In addition to dimethyl ether and fluorocarbons, air is also present in the mixtures and is represented by the origin (i.e., when dimethyl ether and fluorocarbons are zero). It is apparent that drawing a line from any point on the diagram toward the origin represents dilution with air. If the two axes are connected with a diagonal line as shown, that line will represent mixtures of dimethyl ether and fluorocarbons alone. From it the maximum amount of dimethyl ether vapor that can be mixed with fluorocarbon vapor without forming a flammable mixture can be determined.

Consider, for example, the halfway point on the diagonal, which represents a 50:50 vapor mixture of dimethyl ether and fluorocarbon. If a dilution line were drawn from this point toward the origin (which is equivalent to diluting the mixture with air), the line would pass through the flammable area, and the mixture would, therefore, be hazardous. If, however, a dilution line is drawn tangentially to the flammability curve, as shown above, it is possible to determine the maximum amount of dimethyl ether that can be incorporated without producing a flammable mixture at any dilution with air. Such a mixture is represented by the intersection of the dilution line with the diagonal, which occurs at 30 per cent (by volume) dimethyl ether and 70 per cent fluorocarbon 12. Thus, vapor mixtures of dimethyl ether and fluorocarbon 12 will be nonflammable at any air dilution, as long as the initial concentration of dimethyl ether does not exceed 30 per cent by volume.

What does this mean in terms of the liquid phase? For this, a straightforward calculation is made, as follows:

In a closed system, the composition of a vapor mixture of two components can be expressed as:

$$A = \frac{p_1}{P} = \frac{p_1}{p_1 + p_2} \quad (1)$$

where A = Limit in the vapor for the flammable component expressed as a decimal
P = Total pressure
p_1 = Partial pressure of one component
p_2 = Partial pressure of the other component

Applying Raoult's Law:

$$A = \frac{x_1 Po_1}{x_1 Po_1 + x_2 Po_2} = \frac{\left[\frac{\frac{a}{M.W._1}}{\frac{a}{M.W._1} + \frac{b}{M.W._2}}\right] Po_1}{\left[\frac{\frac{a}{M.W._1}}{\frac{a}{M.W._1} + \frac{b}{M.W._2}}\right] Po_1 + \left[\frac{\frac{b}{M.W._2}}{\frac{a}{M.W._1} + \frac{b}{M.W._2}}\right] Po_2} \quad (2)$$

where x_1 = Mole fraction of component one
x_2 = Mole fraction of component two
$M.W._1$ = Molecular weight of component one
$M.W._2$ = Molecular weight of component two
Po_1 = Vapor pressure of component one
Po_2 = Vapor pressure of component two
a = Per cent by weight of component one in the liquid phase
b = Per cent by weight of component two in the liquid phase

Equation (2) simplifies to:

$$A = \frac{\frac{a\ po_1}{M.W._1}}{\frac{a\ po_1}{M.W._1} + \frac{b\ po_2}{M.W._2}} \quad (3)$$

where the symbols have the same significance given above.

since: $a + b = 100$
then: $b = 100 - a$

Substituting in (3):

$$A = \frac{\frac{a\ po_1}{M.W._1}}{\frac{a\ po_1}{M.W._1} + \frac{(100-a)\ po_2}{M.W._2}}$$

Solving for a:

$$a = \frac{100\ A\ M.W._1\ po_2}{M.W._2\ po_1 - A\ (M.W._2\ po_1 - M.W._1\ po_2)} \quad (4)$$

We now have a relationship expressing the concentration limit for the liquid phase (a) in terms of the limit in the vapor phase (A) as determined by flammability studies. Note that all the other terms are constants for any given mixture.

We now substitute in equation (4) the following values for a mixture consisting of dimethyl ether and fluorocarbon 12.

$A = 0.30$ (determined from Figure 1)
po_1 = Vapor pressure of dimethyl ether = 74.7 psia at 70°F.
po_2 = Vapor pressure of fluorocarbon 12 = 84.7 psia at 70°F.
$M.W._1$ = Molecular weight of dimethyl ether = 46.1
$M.W._2$ = Molecular weight of fluorocarbon 12 = 120.9
a = Per cent by weight of dimethyl ether in the liquid phase
b = Per cent by weight of fluorocarbon 12 in the liquid phase

$$a = \frac{100\ (0.30)\ (46.1)\ (84.7)}{(120.9 \times 74.7) - 0.30\ [\ (120.9 \times 74.7) - (46.1 \times 84.7)\ ]}$$

$a = 15.6\%$

This calculation indicates that 15.6 per cent *by weight* is the greatest amount of *liquefied* dimethyl ether that can be mixed with *liquefied* fluorocarbon 12 and not yield a flammable vapor at any dilution with air. To provide a small safety margin, it was decided to adopt a mixture containing 15.0 per cent by weight liquid dimethyl ether for further exploration.

Fractionation

Since dimethyl ether and fluorocarbon 12 differ in boiling points, there was a possibility that the vapor composition might change if a small leak should develop in a container in which the mixture is present. This would give rise to efficient fractionation and the possibility that dimethyl ether could, at some stage, exceed the 30 per cent limit in the vapor phase. To explore such a possibility, fractionation tests were run at various temperatures as described in the experimental section. In essence, the procedure consisted of allowing the mixture to bleed slowly from a container and following changes in the vapor composition with a gas chromatograph. It should be borne in mind that fractionation occurs only when leaks develop and allow the vapor composition to change; it does not occur in normal use, such as withdrawal of propellant from a storage tank.

Table I. Fractionation Data for Mixture Consisting of 15% Dimethyl Ether and 85% Fluorocarbon 12

Per cent by weight of sample discharged	Dimethyl ether in vapor, per cent by volume
A. At room temperature (20°C.)	
0.0	26.7
1.0	26.9
9.8	26.3
27.6	26.2
47.2	26.7
51.8	26.9
72.3	28.2
80.5	27.5
93.5	32.7
97.0	33.6
B. At 0°C.	
0.0	27.6
19.4	26.8
52.8	26.8
65.0	27.3
92.5	32.2
99+	34.8
C. At —10°C.	
0.0	24.1
28.6	24.5
33.4	25.0
77.8	25.3
99.0	33.5
D. At —22°C.	
0.0	23.2
42.0	26.3
77.4	28.7
88.4	37.1
E. At —42°C.	
0.0	27.1
24.6	26.6
32.5	25.3
68.8	22.5
77.8	24.4
86.7	26.9
92.0	25.7
98.0	30.3

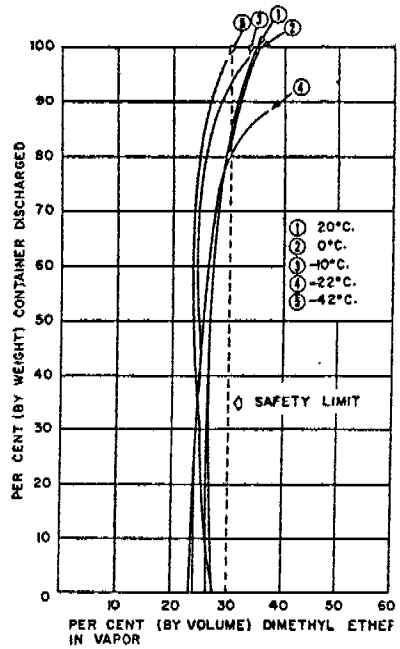

Figure 2. Fractionation curves for mixture consisting of 15% dimethyl ether and 85% fluorocarbon 12.

The data for the fractionation tests are given in Table I and are pictured graphically in Figure 2. The vertical axis in Figure 2 represents the per cent of the container discharged, and the horizontal axis represents the dimethyl ether content of the vapor. The safety limit is at 30% dimethyl ether, determined from Figure 1 as discussed above. Runs were made at five different temperatures to determine the behavior of the blend under conditions of both pressure filling and cold filling. Note that the initial points on the horizontal axis represent the vapor composition of the blend before fractionation begins, *and also represent experimental proof of the calculation above.* The amount of

dimethyl ether in the vapor is actually a little less than might be expected from Raoult's Law.

It can be seen from Figure 2 that fractionation varies with temperature, and that at about 80% of container discharge the dimethyl ether builds up in the vapor in excess of the safety limit. This means that if a slow leak developed in a storage tank of the blend, for example, the vapor coming from the tank after 80% of the contents had bled off would contain greater than 30% dimethyl ether and would, therefore, be flammable. What is needed here is a "tail" to retard the separation of dimethyl ether as discussed above. (Fluorocarbon 12 forms the "head"). Although fluorocarbon 114 could serve as the "tail," it is expensive and would be ruled out on an economic basis if more than two or three per cent were required. The only other alternative is fluorocarbon 11, and the amount to be added must be carefully considered. A sufficient quantity must be present to suppress the buildup of dimethyl ether, but an excess would lower the pressure of the blend, thus requiring more propellant to obtain a given pressure when it is mixed with a product. It was decided to repeat the fractionation tests with a mixture consisting of 10% by weight liquid fluorocarbon 11, 15% dimethyl ether and 75% fluorocarbon 12. The data for the tests are given in Table II and are shown graphically in Figure 3.

Table II. Fractionation data for mixture consisting of 15% dimethyl ether, 75% fluorocarbon 12 and 10% fluorocarbon 11

Per cent by weight of sample discharged	Dimethyl ether in vapor, per cent by volume	Propellant 11 in vapor, per cent by volume
A. At room temperature (20°C.)		
0.0	27.2	2.8
28.6	26.7	3.5
56.6	26.3	5.4
69.5	26.5	9.4
80.0	25.3	10.6
86.2	25.6	16.8
99.0	9.1	79 9
B. At 0°C.		
0.0	25.4	2.4
26.7	26.3	3.2
42.7	25.6	4.0
76.3	26.9	10.6
92.7	25.1	28.1
C. At —10°C.		
0.0	25.8	2.1
25.0	25.2	2.8
36.8	25.2	3.3
50 3	26.0	3.7
68.2	25.8	5.6
96.5	23.9	36.5
D. At —22°C.		
0.0	24.7	1.9
20.2	24.7	2 7
38.6	25.2	2.9
52.7	25.5	4.3
82 4	27.5	8.7
99.0+	28.5	6.3
E. At —42°C.		
Not enough came out of the container to get measurements in a reasonable time.		

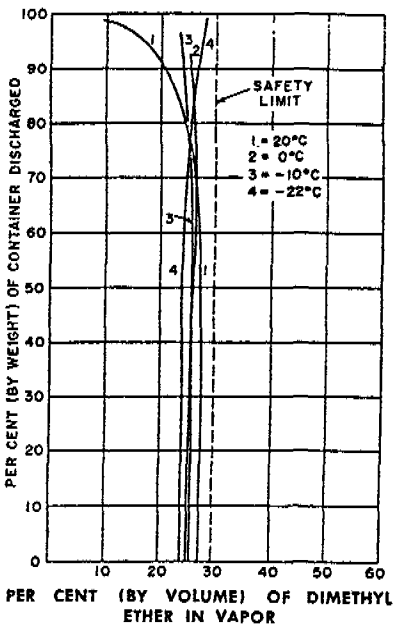

Figure 3. Fractionation curves for mixture of 15% dimethyl ether, 75% fluorocarbon 12 and 10% fluorocarbon 11.

It can be seen from Figure 3 that the fluorocarbon 11 pulled all of the curves away from the safety limit, and the blend will not form a flammable mixture upon dilution with air even if leaks (and, thereby, fractionation) should occur.

Flammability Again

The curve in Figure 1 applied to mixtures of dimethyl ether and fluorocarbon 12. Fluorocarbon 11 has now been added, however, and the data in Table II show that fluorocarbon 11 does build up in the vapor. It was necessary, therefore, to determine what effect this would have on the flammability curve and, hence, on the 30% safety limit.

The fractionation data in Table II show that fluorocarbon 11 in the vapor ranged from a low of 1.9% by volume to a high of 36.5%. At one point a concentration or 79.9% was reached, but at the same time the dimethyl ether content had dropped off to 9%, and this point can be neglected in determining the fluorocarbon ratio to be investigated. It was decided to obtain flammability curves for dimethyl ether with fluorocarbon 12/11 90/10 and 50/50 vapor mixtures, in order to cover the range in which fluorocarbon 11 might be expected to be present.

A flammability tester was constructed according to information available from the Bureau of Mines (4, 5) and is described in the experimental section. In essence, the tester consists of an explosion tube 150 cm in length in which the mixture of gases under test are subjected to ignition from a hot spark. If the mixture is flammable, a flame will be set off and traverse the length of the tube.

The flammability curves which were obtained with the tester are shown in Figure 4. The inner curve applies to fluorocarbon 12/11 90/10 and is identical to Figure 1 which, in turn, applies to straight fluorocarbon 12. In other words, the presence of 10% fluorocarbon 11 in the vapor does not change the flammability curve at all. When fluorocarbon 11 is increased to 50%, however, as shown by the outer curve in Figure 4, the flammable area is enlarged. This is in accordance with the Bureau of Mines' hypothesis that the efficiency of a flammability suppressant depends on the specific heat, since fluorocarbon 11 has a slightly lower specific heat (0.135 cal/g/°C.) than fluorocarbon 12 (0.145 cal/g/°C.). Note, however, that the intersection of the dilution line with the diagonal is only slightly altered, changing the safety limit from 30% dimethyl ether to 28%. Thus, even a relatively large amount of fluorocarbon 11 in the vapor does not affect the safety of the blend.

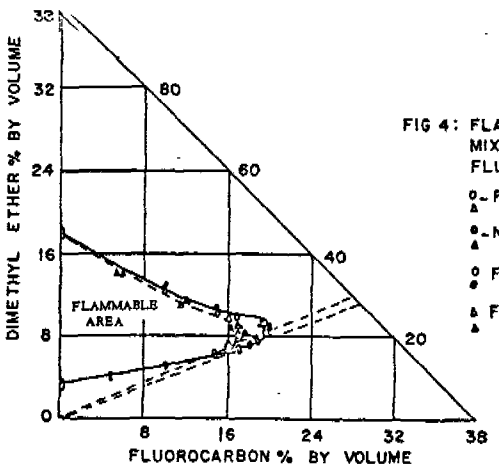

FIG 4: FLAMMABILITY CURVES FOR VAPOR MIXTURES OF DIMETHYL ETHER AND FLUOROCARBON 12/11

- ○- ▲- FLAMMABLE
- ●- ▲- NONFLAMMABLE
- ○ ● FLUOROCARBON 12/11 50/50
- ▲ ▲ FLUOROCARBON 12/11 90/10

PART II

Performance Factors

Expansion Ratio and Pressure: The expansion ratio of a liquified gas is the ratio of the specific volume of the vapor to the specific volume of the liquid. It is indicative of the amount of "breakup" that might be expected from a given propellant. Since dimethyl ether has a considerably higher expansion ratio (350) than fluorocarbon 12 (255), it might be expected that the blend would contribute more "breakup" than an equivalent amount of fluorocarbon 12. This can be calculated as follows:

$$\% \text{ additional "breakup"} = \frac{E_1 a - 0.1\, E_1 a}{E_2} \times 100$$

where E_1 = Expansion ratio of dimethyl ether = 350
E_2 = Expansion ratio of fluorocarbon 12 = 255
a = Concentration (% by weight) of dimethyl ether = 15

The second term in the numerator is a correction for the 10% fluorocarbon 11 and, to apply the most restrictive conditions, assumes that the fluorocarbon 11 detracts only from the dimethyl ether expansion ratio. Substituting numerical values, we have:

$$\% \text{ additional "breakup"} = \frac{350 \times 0.15 - 0.1 \times 0.15 \times 350}{255} \times 100 = 18.5$$

This, theoretically, means that approximately 16% less of the blend should be required to obtain a "breakup" equivalent to that of fluorocarbon 12. However, the blend has a pressure of 64 psig, and more will be required to obtain a given pressure with a product calculated as follows:

$$\% \text{ additional propellant required to offset reduced pressure} = \frac{70 - 64}{70} \times 100 = 9.0$$

Adding the two factors, the advantage of the higher expansion ratio and the disadvantage of lower pressure, we have:

	−9%
	16%
Net gain =	7.0%

Thus, theoretically at least, approximately 7% less of the blend should be required to obtain the spray characteristics equivalent to those of fluorocarbon 12. In actual practice, however, this will have to be evaluated with each individual product, since no account has been taken here of viscosity, evaporation rate and, in the case of paints, the resin or resins being used.

Solvent Properties: Dimethyl ether has a K-B value of 91, fluorocarbon 12 has a value of 18, and the blend has a value of 31. Thus, the blend should have better solvent properties for aerosol paints than straight fluorocarbon 12. This was borne out in tests with nitrocellulose and acrylic lacquers.

The data obtained with nitrocellulose systems are shown in Table III. Although alkyd resins are normally used in commercial lacquers, they were omitted here because they are used in so many different combinations, and it is the tolerance of the nitrocellulose itself for the propellants which is the point of interest.

It can be seen from Table

Table III. Evaluation of Dimethyl Ether-Fluorocarbon Blend with Nitrocellulose Lacquer

Components of Test Solution, Per Cent by Weight			Appearance of Test Solution When Mixed 1:1 by Weight	
Nitrocellulose	Solvent*	Toluene Diluent	With Fluorocarbon 12	With Dimethyl Ether Blend
12	88	0	—	Clear
12	78	10	—	Clear
12	68	20	Clear	Clear
12	58	30	Clear	Clear
12	53	35	Slightly Cloudy	Clear
12	48	40	Very Cloudy	Clear
12	38	50	—	Slightly Cloudy
12	28	60	—	Very Cloudy

* Methylisobutyl Ketone = 80% Isopropanol = 5%
Butyl CELLUSOLVE = 10% Ethanol = 5%

* Paper presented Dec. 6, 1961 during 48th annual meeting, Chemical Specialties Manufacturers Assn., Ntw York.

111 that with fluorocarbon 12, the test solution became cloudy at 35% toluene. With the blend, the cloud point was raised to 50% toluene. This suggests the possibility that some of the active solvent might be replaced with lower cost diluent when the blend is used, but this must be balanced with the evaporation rate of the solvent system and the viscosity of the lacquer solution. Again, each product should be evaluated individually.

In the case of acrylic lacquers, most of those now on the market consist of a solution of resin in toluene. There has not been a great problem in packaging such lacquers as far as resin compatibility is concerned, but it was of interest to determine if an acrylic resin had a greater tolerance for the blend than for the straight fluorocarbon.

The amount of propellant required to cloud 10 grams of a solution consisting of 20% "Acryloid" B-82 and 80% toluene was:

Fluorocarbon 12	*Dimethyl Ether Blend*
13.8 grams	24.4 grams

Thus, with acrylic lacquers, almost twice as much of the blend can be tolerated. This provides a leeway for the filler and formulator, and might permit an increase in solids content if such were desirable from a marketing and performance standpoint.

Summary

Vapor mixtures of dimethyl ether and fluorocarbon 12 are nonflammable as long as the dimethyl ether content is below 30% by volume. This requires a liquid mixture containing no more than 15.6% dimethyl ether by weight, and a blend consisting of 15% dimethyl ether and 85% fluorocarbon propellant 12 was selected for further study.

It was found that, during the latter stages of an efficient fractionation, the vapor from the blend could become flammable from build-up of dimethyl ether. This was due mainly to the difference in boiling points. The addition of 10% fluorocarbon 11 to the blend prevented this buildup, and the dimethyl ether content of the vapor at no time crossed the 30% safety limit.

A blend consisting of 15% by weight dimethyl ether, 75% fluorocarbon 12 and 10% fluorocarbon 11 is a suitable aerosol propellant for high pressure applications, and is safe for use in both pressure filling and cold filling.

Experimental

Flammability Studies: The Bureau of Mines Flammability Tester which was used in this work is shown in Figure 5 and its operation is described in detail in the Bureau's Report of Investigations 4839 (5).

The operation of the instrument was as follows:

1. The tube was sealed and the system evacuated for 30 minutes to remove moisture and reaction products from previous explosions.

2. Sample gases were fed into the system through three-way valves. The amounts were controlled by pressure readings taken on the manometer which was graduated to 0.5 mm. The amount of each gas is given by the relationship:

$$\text{Per cent by volume of sample} = \frac{p}{P}$$

where p = pressure of the sample
P = barometric pressure = total pressure

After the dimethyl ether and fluorocarbon were in, the system was brought to atmospheric pressure by allowing air to enter the tube.

3. After atmospheric pressure was reached, the gases were mixed with the diaphragm pump for five minutes.

4. The pump was then turned off, the glass plate removed from the bottom of the tube and, simultaneously, a spark applied across the gap. If the mixture were flammable, a flame would be set off and travel the length of the tube. The Bureau of Mines is of the opinion that if the flame travels only two-thirds the length of the tube or less, the mixture is non-

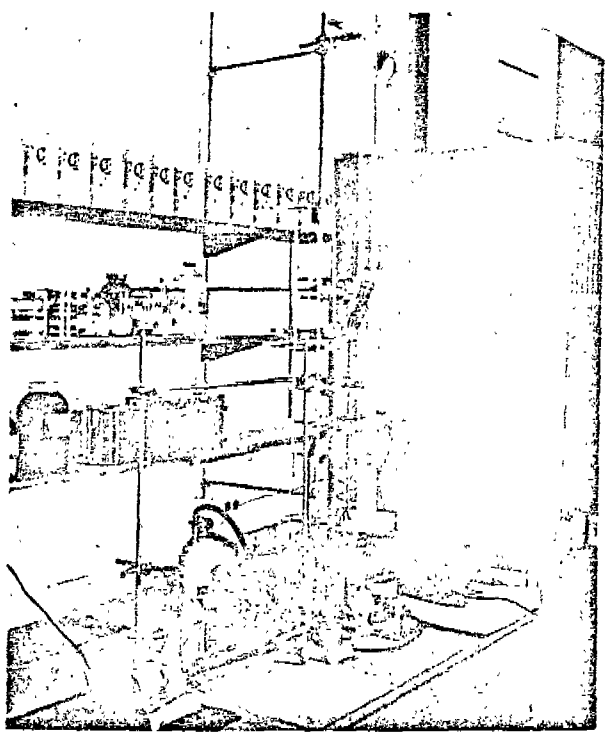

Figure 5. Flammability tester used in developing dimethyl ether fluorocarbon blend.

flammable, and this classification was followed. In practice, our flames either traveled the length of the tube or less than halfway, and there was no difficulty in classifying the mixtures.

Fractionation Studies: The fractionation tests consisted of bleeding off the vapor from containers filled with dimethyl ether blends and following changes in the vapor composition as the containers were emptied. To produce an efficient fractionation, the containers were bled at a minimum rate of 25% in two hours; most of the data in Tables I and II were obtained at the rate of about 25% in three to four hours.

The procedure was as follows: Six-ounce containers were sealed with tilt valves and pressure filled with the mixture being studied. A .046" hole was drilled into actuator buttons and capillary tubes inserted into the holes. Screw clamps were placed on the capillary tubes and the assembly placed on the valves. With the buttons secured in a tilted position, the containers were allowed to bleed off, the rate being controlled by the screw clamps. The containers being run at low temperatures were placed in Dewar flasks filled with the appropriate cryogenic solution.

As the containers were bleeding off, weight losses were determined at periodic intervals and, simultaneously, the vapor composition determined with the gas chromatograph.

It was found in early work that taking samples by bleeding into evacuated containers and then analyzing gave widely varying results and such a method is not recommended.

Acknowledgments

The authors wish to express their appreciation to Mr. M. W. Ranney and Miss C. J. Doherty of the Union Carbide Chemicals technical service laboratory for the extended chromatographic analyses and assistance in determining the solvent properties of the blend, and to Mr. S. S. Taylor for assistance in obtaining flammability data.

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Appendix B

VINYL CHLORIDE/FLUOROCARBON AEROSOL PROPELLANT BLEND

By

R. J. Scott And R. R. Terrill

Technical Service Laboratory

Union Carbide Corporation

Chemicals Division

Tarrytown, New York

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Introduction

FOR some time, one of the top priority projects at the Tarrytown, N. Y., Technical Service Laboratory of Union Carbide Chemicals Co. has been development of propellant blends that would be *both* safe and non-flammable.

The first phase of the project was to develop a high pressure propellant blend. To accomplish this, it was necessary to separate the different candidates according to boiling point and vapor pressure. An example of why these factors are important is the experimental work done with isobutane. This material would not make a good blend with fluorocarbon 12, because it lowers the pressure and tends to separate, producing a flammable vapor. With fluorocarbon 12/11 blended in equal amounts, however, the pressure is not significantly changed, and the vapor coming off at the beginning and the end of a fractionation is rich in fluorocarbon at all times. In other words, there is what might be called a "head and tail" arrangement, with non-flammable fluorocarbon coming off before, with and after the flammable component. Such an arrangement is necessary with all propellant blends involving flammable materials and significant differences in boiling points.

Much research was accomplished on high pressure blends. It was intended that these products could be used as a substitute for straight fluorocarbon 12, which of course, finds application primarily in aerosol paints.

Dimethyl ether is a prime candidate because of its pressure (60 psig. at 70°F), its boiling point (—24°C), and its high K-B value (91).

An equally important research project conducted at the Tarrytown laboratories was the development of *moderate* pressure propellants and propellant blends, which now utilize mixtures of fluorocarbon 12 and 11 in products such as hair sprays, insecticides, and room deodorants. The most common, a 50-50 mixture, has a vapor pressure of 37 psig at 70°F, and there are not many liquifiable gases with vapor pressures falling in this range. One that does is vinyl chloride with a vapor pressure of 35 psig at 70°F and a boiling point of —13.4°C.

Vinyl chloride reportedly has been used by itself as a propellant[23] and mixtures with fluorocarbons have been mentioned[2], but there is no evidence in the published literature that a quantitative blend has been worked out. This paper presents the results of a detailed study on vinyl chloride-fluorocarbon mixtures, which was carried out in the Union Carbide's Technical Service Laboratory, and which led to the development of a safe, nonflammable blend.

Flammability Studies

Unlike dimethyl ether-fluorocarbon mixtures, where one of the flammability curves was known[1], the vinyl chloride curves could not be found in the literature and had to be determined experimentally. In such a case, it is easier to operate a flammability tester with a mixture of two gases rather than three. Accordingly, the curve was located with vapor mixtures of vinyl chloride and fluorocarbon 12, and the effect of added fluorocarbon 11 then determined. The question of what fluorocarbon ratio to use for the vapor was resolved by considering the vapor-liquid equilibria. It can be calculated that the fluorocarbon portion of the liquid phase would have to contain more than 70% fluorocarbon 11 to produce a 50/50 ratio in the vapor. Therefore, a *vapor* ratio of 50/50 would represent the probable maximum that a 50/50 *liquid* ratio would produce. Fractionation tests later showed this to be the case.*

The flammability curves are shown in Figure 1 and

* The apparatus, procedure and technique used for the flammability and fractionation studies were the same as those used for dimethyl ether, and have been described previously[1].

are interpreted in the same manner as those for dimethyl ether[1]. The maximum amount of vinyl chloride that can be tolerated in the vapor is determined by drawing dilution lines tangent to the flammability curves, as shown. The intersection of the dilution lines with the diagonal gives the maximum amounts of vinyl chloride that can be present without forming flammable mixtures at any dilution with air.

The curves in Figure 1 are unusual in that they are almost dome shaped. This is due to the wide flammability range of vinyl chloride which tends to "spread out" the curve, and which produces a steep slope on the lower side. This, in turn, gives a high angle to the dilution line and a high intersect on the diagonal. Very large amounts of vinyl chloride can be tolerated in the vapor thereby; a larger amount of admixant, in fact, than was found with any other of the many blends we have studied.

The inner curve of Figure 1 applies to vinyl chloride-fluorocarbon 12 mixtures and the outer curve to vinyl chloride-fluorocarbon 12/11 50/50. The latter shows an effect similar to that observed with dimethyl ether[1], i.e., the tip is extended and the flammable area is somewhat enlarged. This is in accordance with the specific heat relationships observed previously (0.145 cal/g/°C. for fluorocarbon 12 versus 0.135 cal/g/°C. for fluorocarbon 11)[1] and indicates that fluorocarbon 11 is not as good a flammability suppressant as fluorocarbon 12. It is interesting to note that the specific heat effect does not show up until relatively large amounts of fluorocarbon are present (i.e., at the tip of the curve). The angle of the dilution line, however, is not greatly altered and the safety limit for vinyl chloride in the vapor is only reduced from 48 to 45%. Nevertheless, the difference between the two curves is significant in flammability work and shows that chemical homologues do not necessarily function in the same manner nor with the same degree of efficiency. It is not advisable to apply a curve for one mixture to another made up of chemically similar constituents.

For mixtures of vinyl chloride and fluorocarbon 12 the dilution line in Figure 1 indicates that the vapor can contain as much as 48% vinyl chloride without forming a flammable mixture at any dilution with air. A relationship expressing the liquid phase composition in terms of the vapor for a two-component system has been derived previously[1] and can be applied to vinyl chloride-fluorocarbon 12 mixture as follows:

$$a = \frac{100\,A\,M.W._1\,P_{o_2}}{M.W._2\,P_{o_1} - A\,(M.W._2\,P_{o_1} - M.W._1\,P_{o_2})} \qquad (1)$$

Substituting:

$$a = \frac{100(.48)(62.5)(84.7)}{(120.9)(49.7) - 0.48\ (120.9)\ (49.7) - (62.5)(84.7)}$$

$$a = 45\%$$

where: a = Per cent by weight of vinyl chloride in the liquid phase

A = Limit for the vinyl chloride concentration in the vapor = 48%

P_{o_1} = Vapor pressure of vinyl chloride = 49.7 psia at 70°C.

P_{o_2} = Vapor pressure of fluorocarbon 12 = 84.7 psia at 70°C.

$M.W._1$ = Molecular weight of vinyl chloride = 62.5

$M.W._2$ = Molecular weight of fluorocarbon 12 = 120.9

Whence:

$$A = \frac{P_1}{P} = \frac{P_1}{P_1 + P_2 + P_3} \qquad (2)$$

Take out (A)

The above calculation indicates that liquid mixtures of vinyl chloride and fluorocarbon 12 can contain as much as 45% by weight vinyl chloride without the vapor being flammable. This does not take fractionation into account,

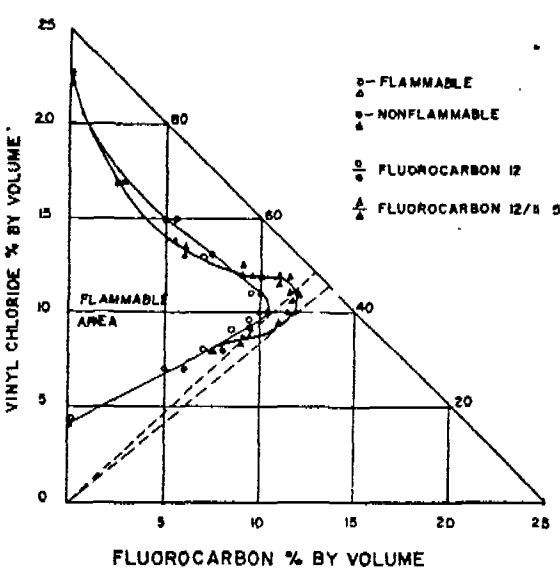

FIG. 1 FLAMMABILITY CURVES FOR VAPOR MIXTURES OF VINYL CHLORIDE AND FLUOROCARBON

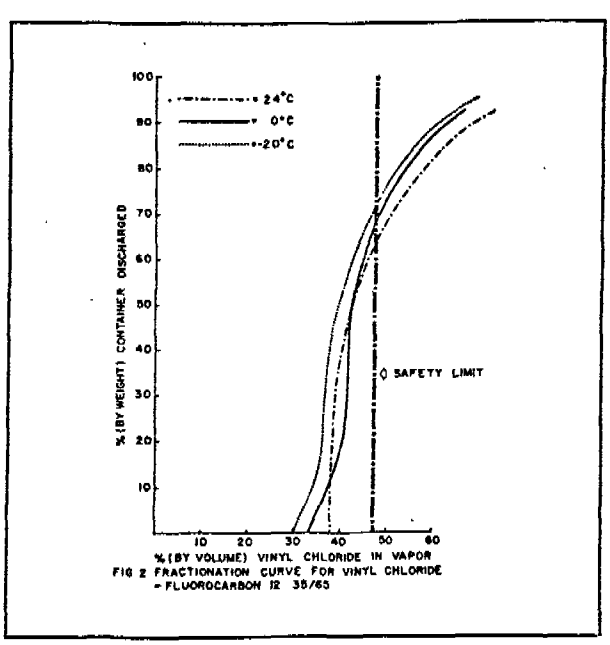

FIG 2 FRACTIONATION CURVE FOR VINYL CHLORIDE - FLUOROCARBON 12 38/63

however, and it will be severe because of the large difference in boiling points and the absence of a "tail"[1]. (See below). When a sufficient amount of fluorocarbon 11 is added to provide a protective "tail," the mixture becomes a moderate pressure blend which is precisely the area now under discussion.

The outer curve in Figure 1 applies to the fluorocarbon 12/11 mixtures in which we are interested. The intersection of the dilution line with the diagonal indicates that, wth a fluorocarbon 12/11 50/50 ratio in the vapor, a maximum of 45% (by volume) vinyl chloride can be tolerated. To convert to the liquid phase is a little more complicated for a system with three components rather than two, but the principle is the same. Let:

A = Limit in the vapor for the flammable component as determined on the flammability chart.
P = Total pressure of the system.
p_1 = Partial pressure of one component.
p_2 = Partial pressure of the second component.
p_3 = Partial pressure of the third component.

Insert (A) Here →X

Applying Raoult's Law:

$$A = \frac{x_1 p_{o_1}}{x_1 p_{o_1} + x_2 p_{o_2} + x_3 p_{o_3}} \qquad (3)$$

$$= \frac{\left[\frac{\frac{a}{M.W._1}}{\frac{a}{M.W._1} + \frac{b}{M.W._2} + \frac{c}{M.W._3}}\right] p_{o_1}}{\left[\frac{\frac{a}{M.W._1}}{\frac{a}{M.W._1} + \frac{b}{M.W._2} + \frac{c}{M.W._3}}\right] p_{o_1} + \left[\frac{\frac{b}{M.W._2}}{\frac{a}{M.W._1} + \frac{b}{M.W._2} + \frac{c}{M.W._3}}\right] p_{o_2} + \left[\frac{\frac{c}{M.W._3}}{\frac{a}{M.W._1} + \frac{b}{M.W._2} + \frac{c}{M.W._3}}\right] p_{o_3}}$$

where: x_1 = Mole fraction of component one
x_2 = Mole fraction of component two
x_3 = Mole fraction of component three
a = Weight per cent of component one in the liquid phase
b = Weight per cent of component two in the liquid phase
c = Weight per cent of component three in the liquid phase
$M.W._1$ = Molecular weight of component one
$M.W._2$ = Molecular weight of component two
$M.W._3$ = Molecular weight of component three
p_{o_1} = Vapor pressure of component one
p_{o_2} = Vapor pressure of component two
p_{o_3} = Vapor pressure of component three

Equation (3) simplifies to:

$$\frac{a\, p_{o_1} M.W._2 M.W._3}{a\, p_{o_1} M.W._2 M.W._3 + b\, p_{o_2} M.W._1 M.W._3 + c\, p_{o_3} M.W._1 M.W._2} \qquad (4)$$

Since a, b, and c are weight percentages, we can say

$$a + b + c = 100$$

and if b = c (i.e., for fluorocarbon 12/11 50/50 in the liquid phase)

then $b = \frac{100 - a}{2} = c$

Substituting,

$$A = \frac{a\, p_{o_1} M.W._2 M.W._3}{a\, p_{o_1} M.W._2 M.W._3 + \left(\frac{100 - a}{2}\right) p_{o_2} M.W._1 M.W._3 + \left(\frac{100 - a}{2}\right) p_{o_3} M.W._1 M.W._2} \qquad (5)$$

Solving for a

$$a = \frac{50 A \left[p_{o_2} M.W._1 M.W._3 + p_{o_3} M.W._1 M.W._2\right]}{p_{o_1} M.W._2 M.W._3 - A\left[p_{o_1} M.W._2 M.W._3 - 1/2 (p_{o_2} M.W._1 M.W._3 + p_{o_3} M.W._1 M.W._2)\right]} \qquad (6)$$

As before[1], we have a relationship expressing the concentration limit in the liquid phase (a), in terms of the limit in the vapor phase (A) as determined by flammability studies. All other terms are constants for any given mixture. Note that careful attention to signs in the denominator is necessary when using this relationship.

The following values can now be substituted in equation (6):

A = 0.45 (from Figure 1)
p_{o_1} = Vapor pressure of vinyl chloride = 49.7 psia at 70°F.
p_{o_2} = Vapor pressure of fluorocarbon 12 = 84.7 psia at 70°F.
p_{o_3} = Vapor pressure of fluorocarbon 11 = 14.7 psia at 70°F.
$M.W._1$ = Molecular weight of vinyl chloride = 62.5
$M.W._2$ = Molecular weight of fluorocarbon 12 = 120.9
$M.W._3$ = Molecular weight of fluorocarbon 11 = 137.4

$$a = \frac{(50)(0.45)\left[(84.7)(62.5)(137.4) + (14.7)(62.5)(120.9)\right]}{(49.7)(120.9)(137.4) - 0.45\left[(49.7)(120.9)(137.4) - \frac{(84.7)(62.5)(137.4)}{2} - \frac{(14.7)(62.5)(170.9)}{2}\right]}$$

$$a = 29.4\%$$

Thus, a mixture consisting of 29.4% by weight of liquefied vinyl chloride and 70.6% of liquefied fluorocarbon 12/11 50/50 contains the maximum amount of vinyl chloride which can be incorporated without forming a flammable vapor.

Since aerosol propellants are used at different temperatures, depending on whether a product is being filled or cold filled, it was necessary to determine the behavior of the blend under fractionation conditions at various temperatures.

Fractionation Studies

As explained previously[1], when the components of an aerosol propellant blend differ in boiling point, there is a possibility that the components *may* separate under conditions of fractionation. Just as in the case of a distillation, the slower the separation is carried out, the more efficient it will be. It was also shown that, under conditions of evaporation, any propellant blend involving a flammable component should have a "head and tail" arrangement, such that protective fluorocarbon vapor comes off before, with, and after the flammable component. An example of an improperly designed blend without this arrangement would be the 45% vinyl-chloride-55% fluorocarbon 12 mixture calculated above. Fractionation tests were run on such a mixture, with the vinyl chloride content reduced to 35% to provide a safety margin. The tests were carried out at various temperatures in the same manner as those for dimethyl ether[1], and the results are shown in Figure 2. The vertical axis represents the per cent of the container discharged, and the horizontal axis represents the vinyl chloride content of the vapor. The safety line is at 48% vinyl chloride, as determined from Figure 1.

It can be seen that all of the curves cross the safety line after about 60% of the container has been discharged. This means that approximately 40% of the amount present will produce a flammable vapor. The shape of the curves in Figure 2 is typical of mixtures which do not

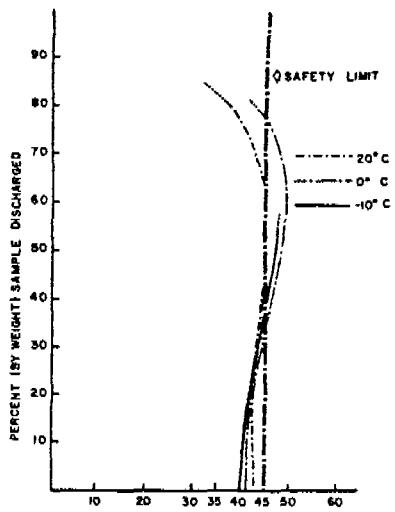

FIG. 3 FRACTIONATION CURVES FOR 27% VINYL CHLORIDE 73% FLUOROCARBON 12/11 50/50

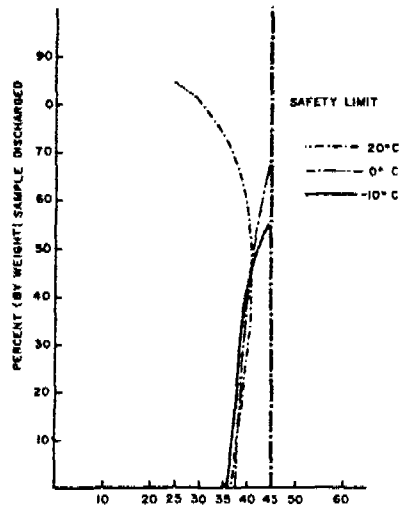

FIG 4 FRACTIONATION CURVES FOR 24% VINYL CHLORIDE 76% FLOROCARBON 12/11 50/50

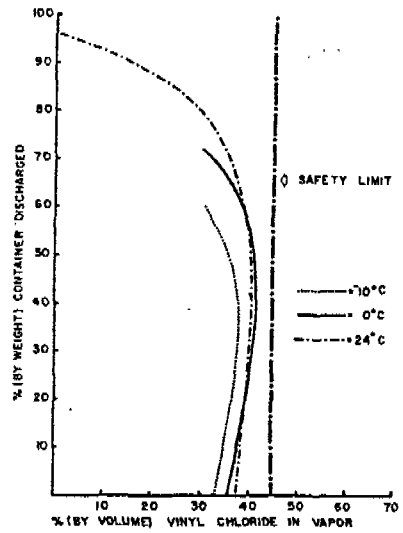

FIG 5. FRACTIONATION CURVES FOR 22% VINYL CHLORIDE 78% FLUOROCARBON 12/11 50/50

have a "head and tail" arrangement, and reducing the amount of flammable material present merely raises the crossover point a little higher.

Returning to fluorocarbon 12/11 mixtures, the calculations given above indicated that a blend consisting of 29% vinyl chloride and 71% fluorocarbon 12/11 50/50 should have a vapor which is nonflammable. It was necessary to examine this mixture also under conditions of fractionation. To allow a safety margin, it was decided to begin fractionation tests with a mixture of 27% vinyl chloride and 73% fluorocarbon 12/11 50/50. The temperatures selected were 20°C., 0°C., and —10°C. Lower temperatures do not allow emergence of enough vapor to get readings in a reasonable time. The fractionation curves are shown in Figure 3. The safety limit is at 45% vinyl chloride, as determined from Figure 1. Note that the points on the horizontal axis represent the initial composition of the vapor and constitute experimental proof of the calculations made above.

It can be seen that even at room temperature (20°C.) the curve approaches the safety line, and at lower temperatures the curves cross over into the flammable area. The latter curves do not extend to complete exhaustion of the container because vapor emission gradually slows and eventually stops at low temperatures. Since a "head and tail" arrangement is already present, the only corrective measure that can be taken is to reduce the amount of vinyl chloride. Accordingly, the tests were repeated on a mixture containing 24% vinyl chloride, as shown in Figure 4. In this case, no curve crosses the safety line but the low temperature curves terminate on it.

A final set of curves was obtained on a mixture containing 22% vinyl chloride, and these are shown in Figure 5. In this case, none of the curves crossed the safety line and the mixture can be regarded as safe for both pressure filling and cold filling.

The final blend, then, consists of 22% by weight vinyl chloride and 78% fluorocarbon 12/11 50/50. The fluorocarbon ratio can be altered and the limits for doing so can be determined. Any mixture different from 50/50, however, should be fractionated to be sure that vinyl chloride does not build up in the vapor.

Performance Factors

Expansion Ratio

Vinyl chloride has an expansion ratio of 333 compared to 255 for fluorocarbon 12 and, presumably, zero for fluorocarbon 11. An interesting calculation can be made on this basis as regards the added "break-up" contributed to an aerosol spray by the presence of vinyl chloride:

Let E_1 = Expansion ratio of vinyl chloride = 333
E_2 = Expansion ratio of fluorocarbon 12 = 255
E_3 = Expansion ratio of fluorocarbon 11 = 0
a_1 = Per cent by weight of vinyl chloride = 22
a_2 = Per cent by weight of fluorocarbon 12 = 39
a_3 = Per cent by weight of fluorocarbon 11 = 39

Then, taking weighted averages:

$$\% \text{ additional "break-up"} = \frac{(E_1 a_1 + E_2 a_2 + E_3 a_3) - (E_2 a_2 + E_3 a_3)}{E_2 a_2 + E_3 a_3} \times 100$$

$$= \frac{333 \times 0.22}{255 \times 0.39} \times 100 = 74 .$$

Thus, theoretically at least, the vinyl chloride blend should require less propellant than a mixture of fluorocarbon 12/11 50/50 to obtain equivalent spray characteristics. This will be limited, however, by the desired evaporation rate, the particular function of the spray and the necessity to replace propellant with concentrate.

Polymerization

It is known that vinyl chloride can be stored for a considerable time without the presence of a polymeriza-

tion inhibitor. It is also known, however, that polymerization is easily initiated by heat, light, oxidizing materials, catalysts, hydrochloric acid, and so on. In view of the many different materials with which an aerosol propellant comes in contact, it is advisable to use a polymerization inhibitor. Three are now in common use: phenol, hydroquinone, and tertiary butyl catechol, in concentrations of 25 to 100 ppm. The most suitable for aerosols use is hydroquinone or the methyl ether thereof.

Packaging Tests

Typical formulations for a hair spray, an insecticide and a room deodorant have been packaged with the vinyl chloride blend. In general, compatibility was excellent and there were indications that the blend may be *less corrosive* to tinplated containers than the straight fluorocarbon propellant. Unlined aluminum containers, however, showed some corrosion in individual cases, and it is recommended that the compatibility of aluminum containers be carefully evaluated before using them with products pressurized with the blend.

Because of the great variety of products utilizing moderate pressure propellants, it is not possible to generalize on the suitability of the blend for each and every one. The blend is safe for use and handling, however, and the economics make an evaluation with any product worthwhile.

SUMMARY

Vapor mixtures of vinyl chloride and fluorocarbon 12/11 50/50 are nonflammable as long as the vinyl chloride content is below 45% by volume. On a liquid-weight basis, this corresponds to 29.4%. Because of fractionation, however, the actual amount of vinyl chloride that can be tolerated is limited to 22%. Because of the high expansion ratio of vinyl chloride, a smaller amount of the propellant blend may be required to produce spray characteristics equivalent to those produced by the straight fluorocarbon. Packaging tests have shown good compatibility with typical products such as hair sprays, insecticides and room deodorants.

A blend consisting of 22% vinyl chloride and 78% fluorocarbon 12/11 50/50 is a suitable aerosol propellant for moderate pressure applications, and is safe for both pressure filling and cold filling. ★

The authors are indebted to M. W. Ranney and Miss C. J. Doherty of the Union Carbide Chemicals Co. Technical Service Laboratory for extensive chromatographic analyses applied to the development of the vinyl chloride blend.

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Appendix C

HYDROCARBON/FLUOROCARBON AEROSOL PROPELLANT BLEND

By

R. J. Scott And R. E. Feathers

Union Carbide Corporation

Chemicals Division

New York

Paper presented by R. J. Scott at the 48th Mid-Year Meeting, Chemical Specialties Manufacturers Association, Chicago, May 15, 1962.

Mr. Scott's at Union Carbide's Technical Service Laboratory, Tarrytown, New York, Mr. Feather's in Atlanta, Georgia.

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A RIGOROUS method of studying aerosol propellant blends has been described previously. (1, 2) This method requires that the flammability diagram for the system being investigated be first constructed from experimental data. The maximum allowable concentration of the flammable component in the vapor is then determined from the diagram, and the corresponding liquid phase equilibrium composition is established by means of a detailed calculation. The liquid phase must then be adjusted, after careful experimentation, to allow for fractionation so as to maintain nonflammability under any conditions of use.

These principles were applied to the development of two propellant blends, one based on dimethyl ether (1) and the other on vinyl chloride. (2) The third area to be investigated was that of hydrocarbon-fluorocarbon combinations. If any such blends were found safe and nonflammable, the relatively low cost of the hydrocarbons could make such mixtures economically attractive. This, the third and concluding treatise of the series, describes the results of our investigation of hydrocarbon-fluorocarbon mixtures.

The present paper, along with those on dimethyl ether and vinyl chloride, report a definitive study of aerosol propellant blends carried on over a period of three years at the Technical Service Laboratory of Union Carbide Chemicals Co. Blends developed on the basis of this study, and currently commercially available, are nonflammable. They cover the major applications involved in aerosol packaging: The dimethyl ether blend serves for high pressure applications, the vinyl chloride blend for moderate pressures and the butane blend (discussed in this paper) for low pressures. Blends for intermediate pressures can be developed, but they should be based on the principles laid down in this study, which form a scientific basis for gauging the safety of any propellant blend.

Three hydrocarbon-fluorocarbon systems were examined, one based on propane for high pressure applications, another on isobutane for moderate pressures and a third on butane for a low pressure blend. The method and experimental equipment were the same as described previously. (1, 2) For convenience, each system will be discussed separately.

Propane-Fluorocarbon

Propane (B. P. = −42° C.) was evaluated for a high pressure blend with fluorocarbon 12 (B. P. = −29.8° C.). In this case fluorocarbon 12 forms the "tail," and it was necessary to find a "head." (1) The only fluorocarbon suitable for this purpose is fluorocarbon 22, which would have to be present in fairly large amounts because of the proximity of its boiling point (−41° C.) to that of propane. In point of fact, propane serves more as a diluent for fluorocarbon 22 than for 12.

We determined the flammability curve with a fluorocarbon 12/22 vapor phase ratio of 50/50 to see how much propane could be tolerated by such a mixture. The flammability curve is shown as the solid line in Figure 1. For comparison, the Bureau of Mines' curve for propane-fluorocarbon 12 is shown as the dotted line. (3) It can be seen that the presence of fluorocarbon 22 not only changes the location of the curve, but also slightly enlarges the flammable area. This is an exception to the general rule that the extinctive efficiency of a gas or vapor is proportional to its specific heat (4), since the specific heat of fluorocarbon 22 (0.152 cal/gm/°C) is higher than that of fluorocarbon 12 (0.145 cal/gm/°C). A similar exception was found by the Bureau of Mines with ethyl mercaptan and fluorocarbon 22 vs. fluorocarbon 12 (5). The anomaly is probably due to the presence of a hydrogen atom in the fluorocarbon 22 molecule.

Figure 1 is interpreted in the same manner as the other flam-

mability diagrams discussed earlier (1, 2). The intersect of the dilution line with the diagonal represents the maximum amount of propane that can be tolerated in the vapor without forming a flammable mixture at any dilution with air. For fluorocarbon 12/22 — 50/50, this amount is 20 per cent by volume.

To determine the corresponding limit in the liquid phase, the relationship for a three component system derived previously is applied (2):

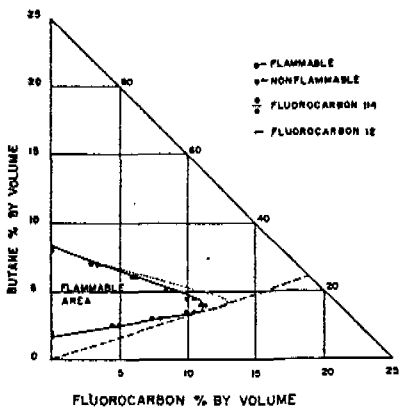


Figure 1

$$A = \frac{ap_{o_1} M.W._2 M.W._3}{ap_{o_1} M.W._2 M.W._3 + bp_{o_2} M.W._1 M.W._3 + cp_{o_3} M.W._1 M.W._2} \quad (I)$$

where:

A=limit in the vapor for the flammable component as determined from the flammability diagram;
a = weight per cent of component one in the liquid phase;
b = weight per cent of component two in the liquid phase;
c = weight per cent of component three in the liquid phase;
p_{o_1}=vapor pressure of component one;
p_{o_2}=vapor pressure of component two;
p_{o_3}=vapor pressure of component three.

Since a, b and c are weight percentages:

$$a + b + c = 100 \quad (II)$$

and, for the system being studied:

c=2.1b (i.e., a vapor phase ratio of fluorocarbon 12/22 50/50 corresponds to a liquid phase ratio of 2.1/1.0). (III)

Substituting equation (III) in equation (II)

$$a + b + 2.1b = 100$$

$$b = \frac{100-a}{3.1} \quad (IV)$$

Substituting equations (III) and (IV) in equation (I)

$$A = \frac{ap_{o_1} M.W._2 M.W._3}{ap_{o_1} M.W._2 M.W._3 + \frac{(100-a)}{3.1} p_{o_2} M.W._1 M.W._3 + 2.1 \frac{(100-a)}{3.1} p_{o_3} M.W._1 M.W._2} \quad (V)$$

Equation (V) now relates the limit for the flammable component in the vapor to the corresponding concentration in the liquid phase. All the other terms are constants for any given mixture. We can now substitute numerical values and solve for "a":

Let A = 0.20 (from Figure 1);
p_{o_1} = vapor pressure of propane = 123.7 psia at 70° F.;
p_{o_3} = vapor pressure of fluorocarbon 22 = 134.7 psia at 70° F.;
p_{o_2} = vapor pressure of fluorocarbon 12 = 84.7 psia at 70 °F.;
$M.W._3$ = molecular weight of propane = 44.1;
$M.W._1$ = molecular weight of fluorocarbon 22 = 86.5;
$M.W._2$ = molecular weight of fluorocarbon 12 = 120.9;

Substituting in equation (V):

$$0.20 = \frac{a\,(123.7)\,(86.5)\,(120.9)}{a\,(123.7)\,(86.5)\,(120.9) + \frac{(100-a)}{3.1}(134.7)\,(44.1)\,(120.9) + \frac{2.1\,(100-a)}{3.1}(84.7)\,(44.1)\,(86.5)}$$

a = 8.0 per cent

Thus, propane has a limit of only 8 per cent by weight in the liquid phase for a safe blend with fluorocarbons 12 and 22 in a ratio of 2/1. This does not take fractionation into account, which previous experience (2) has shown to require some reduction in the flammable component. Furthermore, such a blend would be more expensive than fluorocarbon 12 alone, even though a smaller amount of propellant would be required because of the high pressure of such a combination. Therefore, mixtures of propane and fluorocarbon 12/22 were not investigated any further.

Calculations for mixtures of propane and fluorocarbon 12 alone are of interest because such mixtures are reportedly being used. We apply the relationship derived previously for a two-component system (1), using the dotted line curve in Figure 1 to determine the safe limit for propane in the vapor:

$$a = \frac{100\,A\,M.W._1\,p_{o_2}}{M.W._2\,p_{o_1} - A\,(M.W._2 p_{o_1} - M.W._1\,p_{o_2})}$$

where:

a = safe concentration limit in the liquid phase;
A = limit in the vapor phase = 25 per cent (from Figure 1);
$M.W._1$ = molecular weight of propane = 44.1;
$M.W._2$ = molecular weight of fluorocarbon 12 = 120.9;
p_{o_1} = vapor pressure of propane = 123.7 psia at 70°F.;
p_{o_2} = vapor pressure of fluorocarbon 12 = 84.7 psia at 70°F.

Substituting number values:

$$a = \frac{100\ (0.25)\ (44.1)\ (84.7)}{(120.9)\ (123.7)\ -\ 0.25\ [\ (120.9)\ (123.7)\ -\ (44.1)\ (84.7)\ ]}$$

$a = 7.6$ per cent

Thus, the maximum amount of propane that can be tolerated in a mixture with fluorocarbon 12 is only 7.6 per cent by weight in the liquid phase. This does not take fractionation into account which, with the large spread in boiling points and absence of a "head," is likely to be severe. There is also no allowance for a safety margin which would ordinarily reduce the starting point to about 7.0 per cent. It is, therefore, questionable whether any significantly economical mixture of propane and fluorocarbon 12 can be regarded as nonflammable.

It is interesting to note, in concluding the examination of propane mixtures, that the blend with fluorocarbon 12 had a higher permissible limit in the vapor (25 per cent) than fluorocarbon 22/12 (20 per cent), but a lower limit in the liquid phase (7.6 per cent vs. 8.0 per cent). This is due to the molecular weight and vapor pressure relationships in equations (I) and (II), and points up the necessity of a detailed calculation in going from the vapor to the liquid phase.

Isobutane-Fluorocarbon

Having a vapor pressure of 31 psig at 70°F., isobutane may be regarded as a moderate pressure propellant, and, therefore, a candidate for a blend with fluorocarbon 12/11 - 50/50. Considerable work on isobutane-fluorocarbon 12/11 mixtures (propellant A) (6) had already been carried out by W. H. Reed. However, Dr. Reed had not defined the flammability curve and we had to determine how closely he had approached the safety limit by his method.

Accordingly, flammability data were obtained in the manner described previously (1), and were plotted graphically (Figure 2). An interesting comparison shows that the area inside the curve is smaller than that for propane-fluorocarbon (Figure 1) or for butane-fluorocarbon 12 (Figure 4). Indeed, of all hydrocarbons, isobutane has one of the most favorable flammability curves when incorporated in propellant blends.

In Figure 2, the intersect of the dilution line with the diagonal shows that the safe limit for isobutane in the vapor is 24 per cent by volume. To determine the corresponding composition of the liquid phase, the relationship for a three component system with the fluorocarbons in a 50/50 ratio is used (2) It should be noted that the fluorocarbon ratio is important in these calculations and can change the final form of the relationship:

$$a = \frac{50A\,[p_{o_2}M.W._1M.W._3 + p_{o_3}M.W._1M.W._2]}{p_{o_1}M.W._2M.W._3 - A[p_{o_1}M.W._2M.W._3 - 1/2\,(p_{o_2}M.W._1M.W._3 + p_{o_3}M.W._1M.W._2)]}$$

- a = limit for isobutane in the liquid phase, per cent by weight;
- A = limit for isobutane in the vapor = 24 per cent;
- p_{o_1} = vapor pressure of isobutane = 45.7 psia at 70°F.;
- p_{o_2} = vapor pressure of fluorocarbon 12 = 84.7 psia at 70°.;
- p_{o_3} = vapor pressure of fluorocarbon 11 = 14.7 psia at 70°F.;
- $M.W._1$ = molecular weight of isobutane = 58.1;
- $M.W._2$ = molecular weight of fluorocarbon 12 = 120.9;
- $M.W._3$ = molecular weight of fluorocarbon 11 = 137.4.

Substituting:

$$a = \frac{50\ (.24)\ [\ (84.7)\ (58.1)\ (137.4)\ +\ (14.7)\ (58.1)\ (120.9)\ ]}{(45.7)\ (120.9)\ (137.4)\ -\ 0.24[\ (45.7)\ (120.9)\ (137.4)\ -\ \frac{(84.7)\ (58.1)\ (137.4)}{2}\ \ \frac{(14.7)\ (58.1)\ (120.9)\ ]}{2}}$$

$a = 14.0$

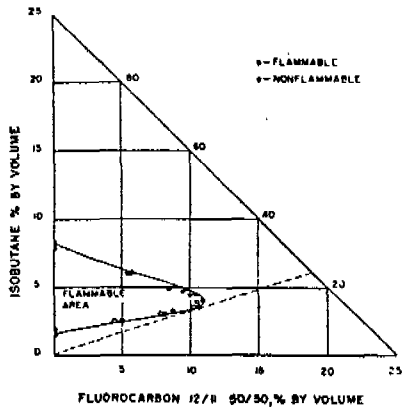


Figure 2

Isobutane, therefore, has the high (for a hydrocarbon) limit of 14 per cent by weight in the liquid phase when mixed with fluorocarbon 12/11—50/50. However, fractionation of the blend is to be expected. Dr. Reed found, by flammability determinations at room temperature, that fractionation lowered the safety limit to approximately 12 per cent, and reduced propellant A even further to 10 per cent to provide a safety margin. It was of interest to determine if this limit was sufficient to cover fractionation at cold filling temperatures. Accordingly, fractionation curves were run on propellant A at five different temperatures, as shown in Figure 3. The lowest was −10° C., since vapor emission at lower temperatures was not sufficient to get readings in a reasonable time. The safety line is the point of intersect of the dilution line with the diagonal in Figure 2.

As can be seen in Figure 3, none of the curves touch or cross the safety line, and propellant A appears equally safe for both cold and pressure filling.

The importance of a proper "head" and "tail" arrangement in any blend comprising components of significantly different boiling

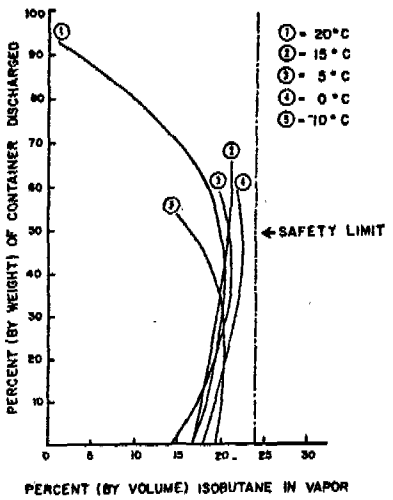


Figure 3

points is shown in Figure 4. We fractionated a blend similar to propellant A., with the isobutane content maintained at 10 per cent, but the fluorocarbon 12/11 ratio changed from 50/50 to 35/65. The amount of fluorocarbon 12 present in this blend is not sufficient to form an adequate "head," and the vapor is flammable at room temperature (curve No. 1 in Figure 4) throughout most of the fractionation. At 10° C. (curve No. 2) the vapor becomes flammable during the middle stages of the fractionation. The curve would probably swing back across the safety line during the latter stages if vapor emission had not ceased due to the low temperature and large amount of fluorocarbon 11 remaining. It cannot be emphasized too strongly that a safe propellant blend must be rigorously devised so that the vapor will remain nonflammable under conditions of use.

Butane-Fluorocarbon

With its vapor pressure of 17 psig at 70° F., butane is a low pressure propellant and a companion to fluorocarbon 114. With boiling points so close together (-0.6° C. for butane and 3.6° C. for fluorocarbon 114), it was assumed that fractionation would present no problem. Accordingly, flammability data were obtained on butane-fluorocarbon 114 mixtures; the curve is plotted in Figure 4. For comparison, the Bureau of Mines' curve for fluorocarbon 12 (3) is shown as the dotted line. It can be seen that fluorocarbon 114 reduces the flammable area considerably, due to the specific heat relationship (0.160 cal/gm/° C. for fluorocarbon 114 vs. 0.145 cal/gm/° C. for fluorocarbon 12). It is also interesting, that the curve for butane - fluorocarbon 114 is strikingly similar to that for isobutane-fluorocarbon 12/11 – 50/50 (Figure 2). If one is superimposed on the other, they appear almost identical.

The intersect of the dilution line with the diagonal in Figure 4 shows that the safe limit for butane in the vapor is about the same for fluorocarbon 12 and 114, at 24 per cent by volume. To determine the corresponding liquid phase composition for a blend of butane and fluorocarbon 114, which would find application in uncoated glass bottles, we apply equation (VI), for a two-component system where:

a = safe concentration limit in the liquid phase, per cent by weight;

A = limit in the vapor phase = 24 per cent (from Figure 4);

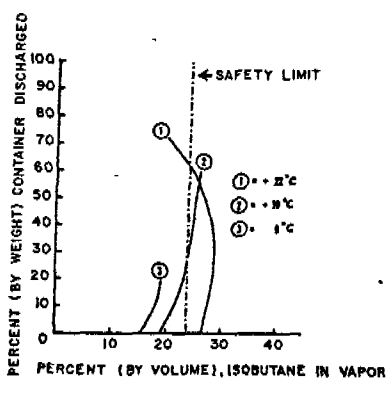
p_{o_1} = vapor pressure of butane = 31.7 psia at 70°F.;

p_{o_2} = vapor pressure of fluorocarbon 114 = 27.7 psia at 70°F.;

$M.W._1$ = molecular weight of butane = 58.1;

$M.W._2$ = molecular weight of fluorocarbon 114 = 170.9.

Figure 4



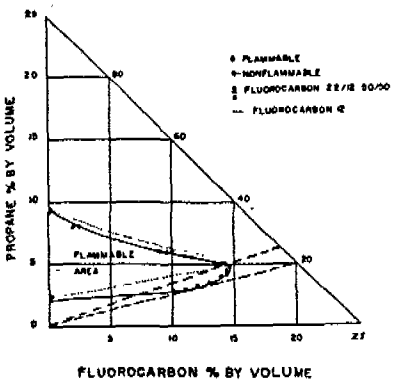


Figure 5

whence:

$$a = \frac{100\,(0.24)\,(58.1)\,(27.7)}{(170.9)\,(31.7) - 0.24[\,(170.9)\,(31.7) - (58.1)\,(27.7)\,]}$$

$$a = 8.5 \text{ per cent}$$

Allowing for a small degree of fractionation, it appears that approximately 6.5 to 7.0 per cent by weight of liquefied butane might safely be incorporated with fluorocarbon 114. However, actual fractionation tests should be run to determine the precise amount. This is disappointing, but in line with other hydrocarbon blends.

Of more commercial importance, perhaps, is a blend of butane with fluorocarbon 12/114–10/90, since the latter is frequently employed with aerosol perfumes. To determine the safe limit for butane in the liquid phase of such a mixture, we apply equation (I) where:

A = limit for butane in the vapor = 0.24;

a = weight per cent of butane in the liquid phase;

b = weight per cent of fluorocarbon 12 in the liquid phase;

c = weight per cent of fluorocarbon 114 in the liquid phase;

p_{o_1} = vapor pressure of bu-

tane = 31.7 psia at 70°F.;

p_{o_2} = vapor pressure of fluorocarbon 12 = 84.7 psia at 70°F.;

p_{o_3} = vapor pressure of fluorocarbon 114 = 27.7 psia at 70°F.;

$M.W._1$ = molecular weight of butane = 58.1;

$M.W._2$ = molecular weight of fluorocarbon 12 = 120.9;

$M.W._3$ = molecular weight of fluorocarbon 114 = 170.9.

Again,

$$a + b + c = 100 \qquad \text{(VIII)}$$

and: $c = 9\,b$ (i.e., for fluorocarbon 12/114 10/90)

whence:

$$b = \frac{100-a}{10} \qquad \text{(IX)}$$

Substituting equations (VIII) and (IX) in equation (I):

$$A = \frac{a p_{o_1} M.W._2 M.W._3}{a p_{o_1} M.W._2 M.W._3 + \frac{(100-a)}{10}(p_{o_2} M.W._1 M.W._3) + 9\frac{(100-a)}{10} p_{o_3} M.W._1 M.W._2}$$

Substituting numerical values and solving for a:

$$0.24 = \frac{a\,(31.7)\,(120.9)\,(170.9)}{a\,(31.7)\,(120.9)\,(170.9) + \frac{(100-a)}{10}[(84.7)\,(58.1)\,(170.9)] + 9\frac{(100-a)}{10}[(27.7)\,(58.1)\,(120.9)]}$$

$a = 11.1$ per cent

Here, we find that the addition of fluorocarbon 12 to fluorocarbon 114 raises the amount of butane that can be tolerated to 11 per cent. This again demonstrates the need for a detailed calculation when translating from the vapor to the liquid phase.

A blend of butane and fluorocarbon 12/114–10/90 is now under development at the Union Carbide Chemicals' Technical Service Laboratory. It is expected to be equivalent in performance to the straight fluorocarbon and will be of considerable economic interest.

Summary

In general, only small amounts of the hydrocarbons can be incorporated with fluorocarbons to produce nonflammable propellant blends. The limits for the various mixtures are as follows:

Blend	Max. flammable component, % by wt. in liquid phase
1. Propane-fluorocarbon 12/22-2.1/1.0	8.0
2. Propane-fluorocarbon 12	7.6
3. Isobutane-fluorocarbon 12/11-50/50	10.0
4. Butane-fluorocarbon 114	8.5
5. Butane-fluorocarbon 12/114-10/90	11.1

Only one of these (No. 3) has been corrected for fractionation. Fractionation can lower the safe limit for some of the other blends considerably, particularly for blends of components with widely divergent boiling points.

A blend of butane and fluorocarbon 12/114 – 10/90 appears to be feasible and is now under development as a low pressure propellant for aerosol perfumes.

Experimental

The apparatus, procedure and technique used for the flammability and fractionation studies were the same as those used for the dimethyl ether blend, and have been described previously. (1)

Acknowledgments

The authors are indebted to T. C. Hower and K. O. Mahler for extensive chromatographic analyses involved in carrying out the fractionation tests discussed in this paper.

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Appendix D

GENERAL EQUATIONS FOR CALCULATING THE COMPOSITION OF AEROSOL PROPELLANT BLENDS OF INTERMEDIATE PRESSURES

By

R. J. Scott

Technical Service Laboratory

Union Carbide Corporation

Chemicals Division

Tarrytown, New York

INTRODUCTION

The UCON® aerosol propellant blends were developed to cover three major products areas: those utilizing high pressures (such as paints), moderate pressures (such as insecticides) and low pressures (such as perfumes). Many products, however, require intermediate pressures, and although it would not be economical to develop a specific blend for each one, it is possible to adjust the pressure of the present blends by adding more fluorocarbon to them. In this way, it is possible to retain the nonflammability of the blend and at the same time provide a price advantage, although it may be less than that of the parent mixture. Therefore, a simple means of calculating the composition of blends with intermediate pressures would be useful in broadening the application of all the blends.

It is the purpose of this report to show how general relationships can be derived for adjusting the composition of any UCON blend to any desired pressure.

SUMMARY AND CONCLUSIONS

The following relationships show the composition required to produce the desired pressure, P', in psia at 70°F. Percentages, molecular weights, and mole fractions are incorporated in the various constants, and care should be taken to be sure the correct relationships are being used for a given mixture:

I. UCON Propellant P:

For lower pressures by dilution with propellant 11:

$$\% \text{ propellant 12} = \frac{52.5P' - 803}{67.3 - 0.32P'}$$

$$\% \text{ dimethyl ether} = \frac{10.5P' - 160}{67.3 - 0.32P'}$$

$$\% \text{ propellant 11} = \frac{7690 - 95P'}{67.3 - 0.32P'}$$

II. UCON Propellant A:

A. For higher pressures by dilution with propellant 12:

$$\% \text{ propellant 12} = \frac{51P' - 1266}{26 + 0.07P'}$$

$$\% \text{ isobutane} = \frac{701 - 8P'}{26 + 0.07P'}$$

$$\% \text{ propellant 11} = \frac{3159 - 36P'}{26 + 0.07P'}$$

B. For lower pressures by dilution with propellant 11:

$$\% \text{ propellant 12} = \frac{31.5P' - 481.5}{33.5 - 0.17P'}$$

$$\% \text{ isobutane} = \frac{7P' - 107}{33.5 - 0.17P'}$$

$$\% \text{ propellant 11} = \frac{3935 - 55.6P'}{33.5 - 0.17P'}$$

III. UCON Vinyl Chloride Blend:

A. For higher pressures by dilution with propellant 12:

$$\% \text{ propellant 12} = \frac{64.7P' - 2170}{21.0 + 0.16P'}$$

$$\% \text{ vinyl chloride} = \frac{1541 - 17.6P'}{21.0 + 0.16P'}$$

$$\% \text{ propellant 11} = \frac{2735 - 31.2P'}{21.0 + 0.16P'}$$

B. For lower pressures by dilution with propellant 11:

$$\% \text{ propellant 12} = \frac{27.3P' - 417.3}{38.4 - 0.26P'}$$

$$\% \text{ vinyl chloride} = \frac{15.4P' - 235.8}{38.4 - 0.26P'}$$

$$\% \text{ propellant 11} = \frac{4493 - 68.6P'}{38.4 - 0.26P'}$$

IV. UCON Fragrance Propellant:

For higher pressures by dilution with propellant 12:

$$\% \text{ propellant 12} = \frac{63.1P' - 1800}{45.7 - 0.096P'}$$

$$\% \text{ n-butane} = \frac{595 - 6.8P'}{45.7 - 0.096P'}$$

$$\% \text{ propellant 114} = \frac{5760 - 66P'}{45.7 - 0.096P'}$$

DISCUSSION

The original blends were designed with "head and tail" arrangements to allow for fractionation during use. If the pressure were changed merely by maintaining the concentration of the flammable component and altering the fluorocarbon ratio, the "head and tail" arrangement would be altered and the mixture could become flammable. On the other hand, if fluorocarbon is added to a blend as such, the flammable component becomes diluted and although the fluorocarbon ratio of the total mixture is changed, the ratio relative to the flammable component is not.

Intermediate pressures, then, can be obtained by the addition of fluorocarbon to one of the standard blends. The calculations below show how each standard blend can be so adjusted.

I. UCON Propellant P (Pressure = 64 psig at 70°F).

The pressures of interest here are those below 64 psig, since propellant P is already a high-pressure blend and there would be no point in making it higher. This means that propellant 11 would be added, and the amount required to obtain any desired pressure can readily be calculated as follows:

Present Composition : 15% (0.326 moles) dimethyl ether
75% (0.620 moles) propellant 12
10% (0.073 moles) propellant 11
Total moles = 1.019

To 100 parts of the blend will be added y parts of propellant 11 to obtain the desired pressure P′, so that the total moles of the new mixture becomes $(1.019 + \frac{y}{137.4})$, and:

$$P' = p_1 + p_2 + p_3 = x_1 p_{o_1} + x_2 p_{o_2} + x_3 p_{o_3} \qquad (1)$$

where: p = partial pressure of the individual components in psia at 70°F

x = mole fraction of a given component

p_o = vapor pressure of the pure component, in psia at 70°F

Subscripts refer to dimethyl ether, propellant 12, and propellant 11, respectively.

Substituting numerical values in equation (1):

$$P' = \frac{(0.326)(74.4) + (0.620)(84.7) + \left(0.073 + \frac{y}{137.4}\right)(14.7)}{1.019 + \frac{y}{137.4}} \qquad (2)$$

$$y = \frac{78.0 - 1.02P'}{0.007P' - 0.107} \qquad (3)$$

Equation (3) shows the additional amount of propellant 11, in the same weight units as used for the other components, required to lower the pressure of UCON propellant P to the new pressure, P'. In examining equation (3), it is obvious that the numerator will always be positive, since P' is decreasing with successive additions of propellant 11. It might at first glance appear possible to have a negative denominator and, hence, a negative value for y. However, the denominator must first become zero upon dilution with UCON propellant 11 (at P' = atmospheric pressure, approximately 15 psia) before it becomes negative. This point would correspond to infinite dilution with propellant 11, and in practical terms the pressure of the mixture would approach that of propellant 11 and never go below it. Thus, a negative value for y would have no physical meaning.

The composition of the resulting mixture is then readily calculated as follows:

$$\% \text{ dimethyl ether} = \left(\frac{15}{100 + y}\right)100 = \frac{10.5P' - 160}{67.3 - 0.32P'}$$

$$\% \text{ propellant 12} = \left(\frac{75}{100 + y} \right) 100 = \frac{52.5P' - 803}{67.3 - 0.32P'}$$

$$\% \text{ propellant 11} = \left(\frac{10 + y}{100 + y} \right) 100 = \frac{7690 - 95P'}{67.3 - 0.32P'}$$

II. UCON Propellant A (Pressure = 37.5):

With UCON propellant A, the pressure adjustment can either be upward with additional propellant 12, or downward with additional propellant 11.

A. For an upward adjustment with propellant 12:

Present Composition: 45% (0.372 moles) propellant 12
10% (0.172 moles) isobutane
45% (0.327 moles) propellant 11

Total moles = 0.871

For the addition of y parts of propellant 12 to 100 parts of the blend to obtain the desired pressure P', the total moles become $(0.871 + \frac{y}{120.9})$, and:

$$P' = x_1 p_{o_1} + x_2 p_{o_2} + x_3 p_{o_3}$$

where the symbols have the same significance as above and the subscripts refer to propellant 12, isobutane and propellant 11, respectively.

Substituting numerical values:

$$P' = \frac{\left(0.372 + \frac{y}{120.9}\right) 84.7 + (0.172)(45.7) + (0.327)(14.7)}{0.871 + \frac{y}{120.9}} \qquad (4)$$

$$y = \frac{0.871P' - 44.16}{0.701 - 0.008P'} \qquad (5)$$

Here, when P' is approximately 51 psia (which is the pressure of propellant A), the numerator becomes zero and no propellant 12 is to be added. As P' increases, the denominator approaches zero at 85 psia, which corresponds to infinite dilution with propellant 12.

The percentage composition of the new mixtures can be expressed as:

$$\% \text{ propellant 12} = \left(\frac{45 + y}{100 + y}\right)100 = \frac{51P' - 1266}{26 + 0.07P'}$$

$$\% \text{ isobutane} = \left(\frac{10}{100 + y}\right)100 = \frac{70i - 3P'}{26 - }$$

$$\% \text{ } = \left(\frac{45}{100 + y}\right)100 \quad \frac{3112 - 3.}{26 + 0.}$$

B. [illegible]

[illegible] becom[illegible]

$$P' = \frac{(0.372)(84.7) + (0.172)(45.7) + \left(0.327 + \frac{y}{137.4}\right)(14.7)}{0.871 + \frac{y}{137.4}} \qquad (6)$$

$$y = \frac{44.16 - 0.871P'}{0.007P' - .107} \qquad (7)$$

The same considerations apply here as with equation (3), i.e., as P' becomes lower, the denominator approaches zero which is equivalent to infinite dilution with propellant 11. It is interesting to note that equations (5) and (7) differ primarily in sign.

The precentage compositions for the lower-pressure mixtures are:

$$\% \text{ propellant 12} = \left(\frac{45}{100 + y}\right)100 = \frac{31.5P' - 481.5}{33.5 - 0.17P'}$$

$$\% \text{ isobutane} = \left(\frac{10}{100 + y}\right)100 = \frac{7P' - 107}{33.5 - 0.17P'}$$

$$\% \text{ propellant 11} = \left(\frac{45 + y}{100 + y}\right)100 = \frac{3935 - 55.6P'}{33.5 - 0.17P'}$$

III. UCON Vinyl Chloride Blend (Pressure = 36.5 psig at 70°F)

As with propellant A, the pressure of the vinyl chloride blend can be adjusted either upward or downward. The downward adjustment is probably of greatest interest, particularly for the large hair spray market, but there may be occasion for an upward adjustment also and calculations for both will be given.

A. For an upward adjustment with additional propellant 12:

Present Composition: 39% (0.323 moles) propellant 12
22% (0.352 moles) vinyl chloride
39% (0.284 moles) propellant 11

Total moles = 0.959

Adding y units of propellant 12 to obtain the desired pressure P', the total moles become $(0.959 + \frac{y}{120.9})$ and:

$$P' = \frac{\left(0.323 + \frac{y}{120.9}\right)(84.7) + (0.352)(49.7) + (0.284)(14.7)}{0.959 + \frac{y}{120.9}} \qquad (8)$$

$$y = \frac{0.959P' - 49.1}{0.701 - 0.008P'} \qquad (9)$$

The same considerations apply here as with equation (5). The percentage composition of the higher-pressure mixture is:

$$\% \text{ propellant 12} = \left(\frac{39 + y}{100 + y}\right)100 = \frac{64.7P' - 2170}{21.0 + 0.16P'}$$

$$\% \text{ vinyl chloride} = \left(\frac{22}{100 + y}\right)100 = \frac{1541 - 17.6P'}{21.0 + 0.16P'}$$

$$\% \text{ propellant 11} = \left(\frac{39}{100 + y}\right)100 = \frac{2735 - 31.2P'}{21.0 + 0.16P'}$$

B. For a downward adjustment with propellant 11:

$$P' = \frac{(0.323)(84.7) + (0.352)(49.7) + \left(0.284 + \frac{y}{137.4}\right)14.7}{0.959 + \frac{y}{137.4}} \qquad (10)$$

$$y = \frac{49.1 - 0.959P'}{0.007P' - 0.107} \qquad (11)$$

The percentage compositions of the lower-pressure mixtures are:

$$\% \text{ propellant 12} = \left(\frac{39}{100 + y}\right)100 = \frac{27.3P' - 417.3}{38.4 - 0.26P'}$$

$$\% \text{ vinyl chloride} = \left(\frac{22}{100 + y}\right)100 = \frac{15.4P' - 235.8}{38.4 - 0.26P'}$$

$$\% \text{ propellant 11} = \left(\frac{39 + y}{100 + y}\right)100 = \frac{4493 - 68.6P'}{38.4 - 0.26P'}$$

IV. UCON Fragrance Propellant (Pressure = 20 psig at 70°F)

This blend is a low-pressure propellant, and the only adjustment of interest would be an increase in pressure with propellant 12:

Present Composition: 9.15% (0.076 moles) propellant 12
8.50% (0.146 moles) butane
82.35% (0.482 moles) propellant 114
Total moles = 0.704

$$P' = \frac{\left(0.076 + \frac{y}{120.9}\right)84.7 + (0.146)(31.7) + (0.482)(27.7)}{0.704 + \frac{y}{120.9}} \qquad (12)$$

$$y = \frac{0.704P' - 24.4}{0.701 - 0.008P'} \qquad (13)$$

The percentage compositions of the new mixtures become:

$$\% \text{ propellant 12} = \left(\frac{9.15 + y}{100 + y}\right)100 = \frac{63.1P' - 1800}{45.7 - 0.096P'}$$

$$\% \text{ n-butane} = \left(\frac{8.5}{100 + y}\right)100 = \frac{595 - 6.8P'}{45.7 - 0.096P'}$$

$$\% \text{ propellant 114} = \left(\frac{82.35}{100 + y}\right)100 = \frac{5760 - 66P'}{45.7 - 0.096P'}$$

Appendix E

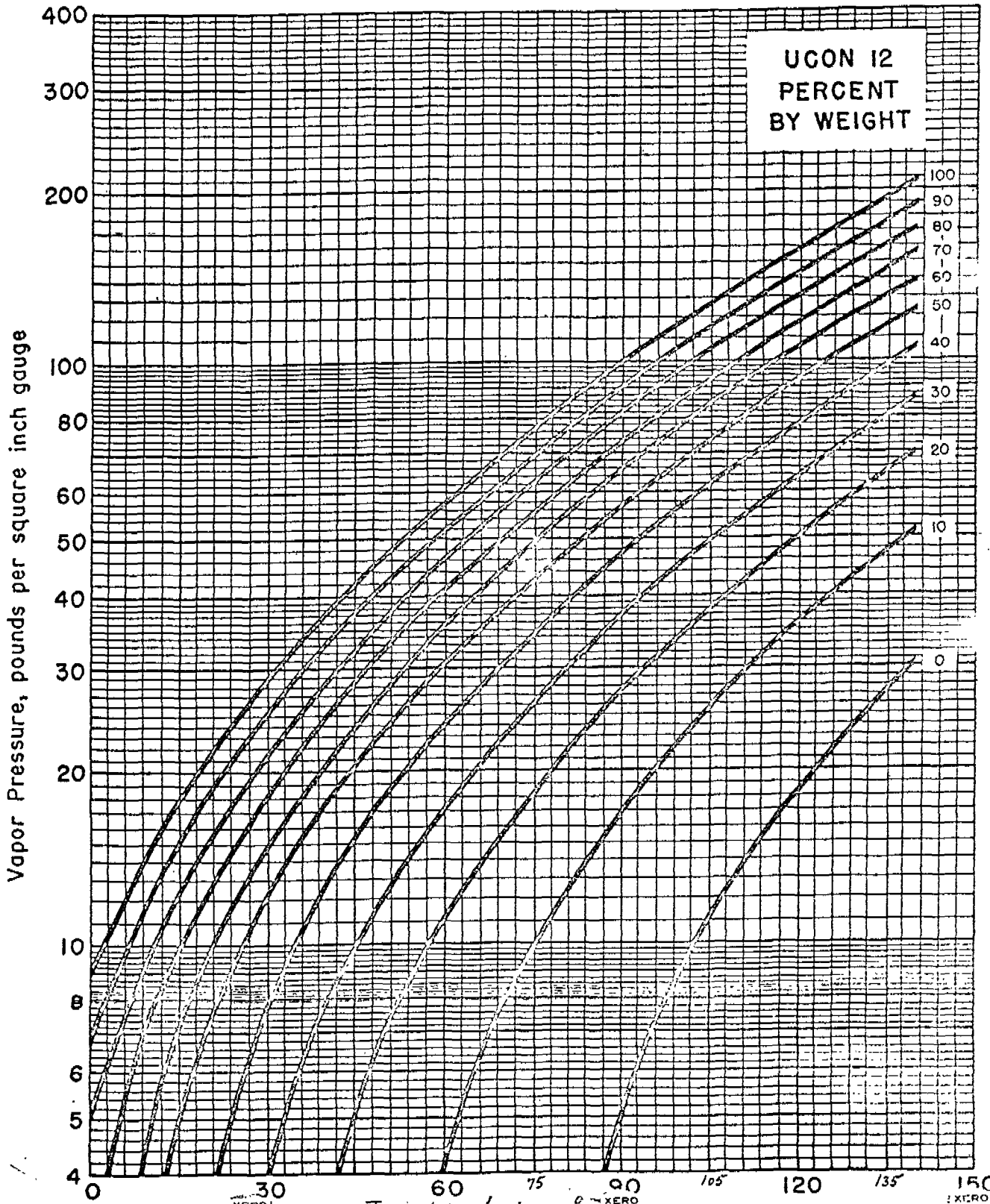
UCON Propellant 12/11

VAPOR PRESSURE VS. TEMPERATURE

Appendix E

UCON® 12/UCON® 11 Fluorocarbon Propellant Blends

Vapor Pressure vs Temperature, °F



Appendix F

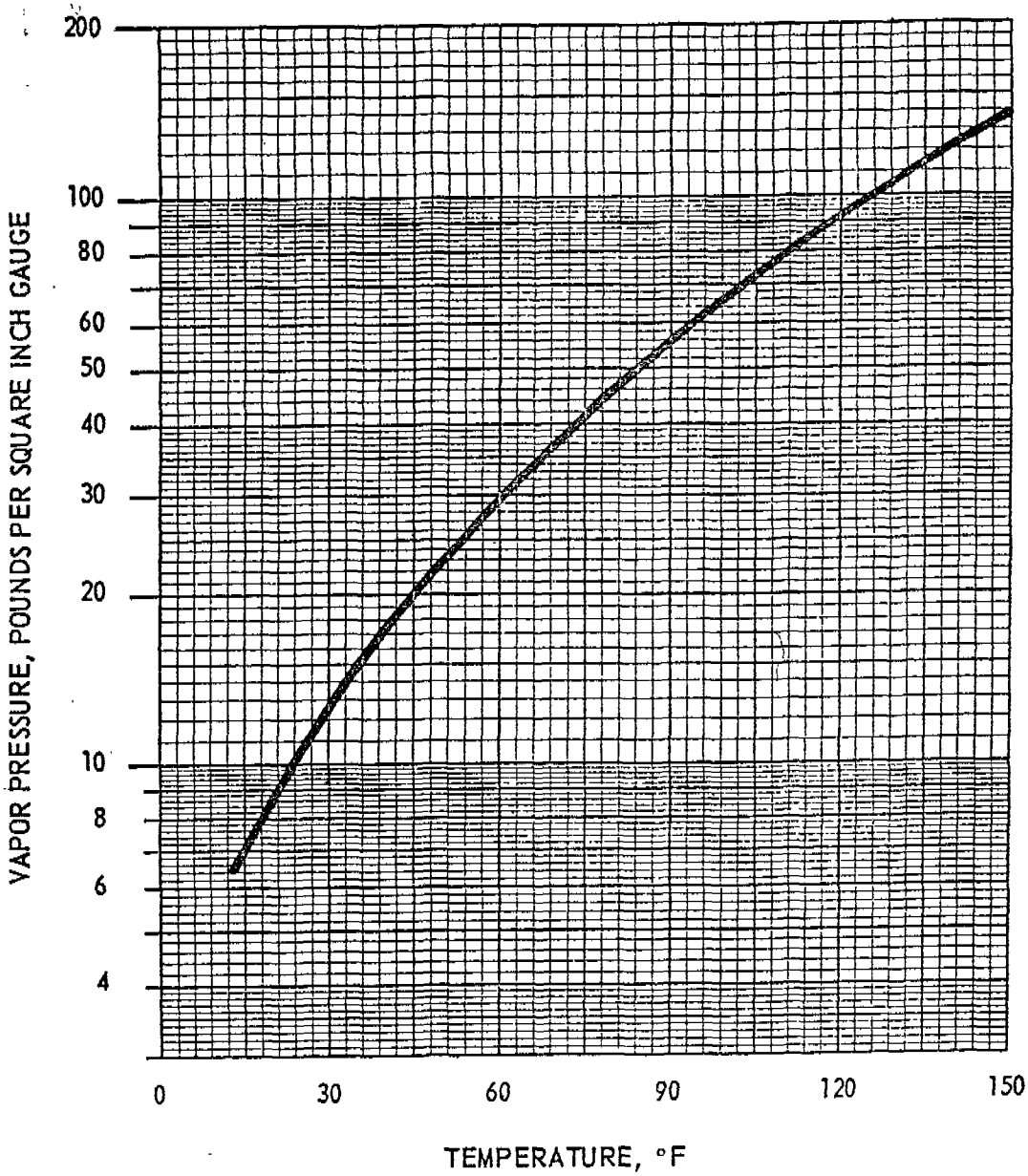
UCON Propellant A and Vinyl Chloride Blend .

VAPOR PRESSURE VS. TEMPERATURE

Appendix F

UCON® PROPELLANT A AND VINYL CHLORIDE BLEND

VAPOR PRESSURE VS TEMPERATURE, °F



Appendix G

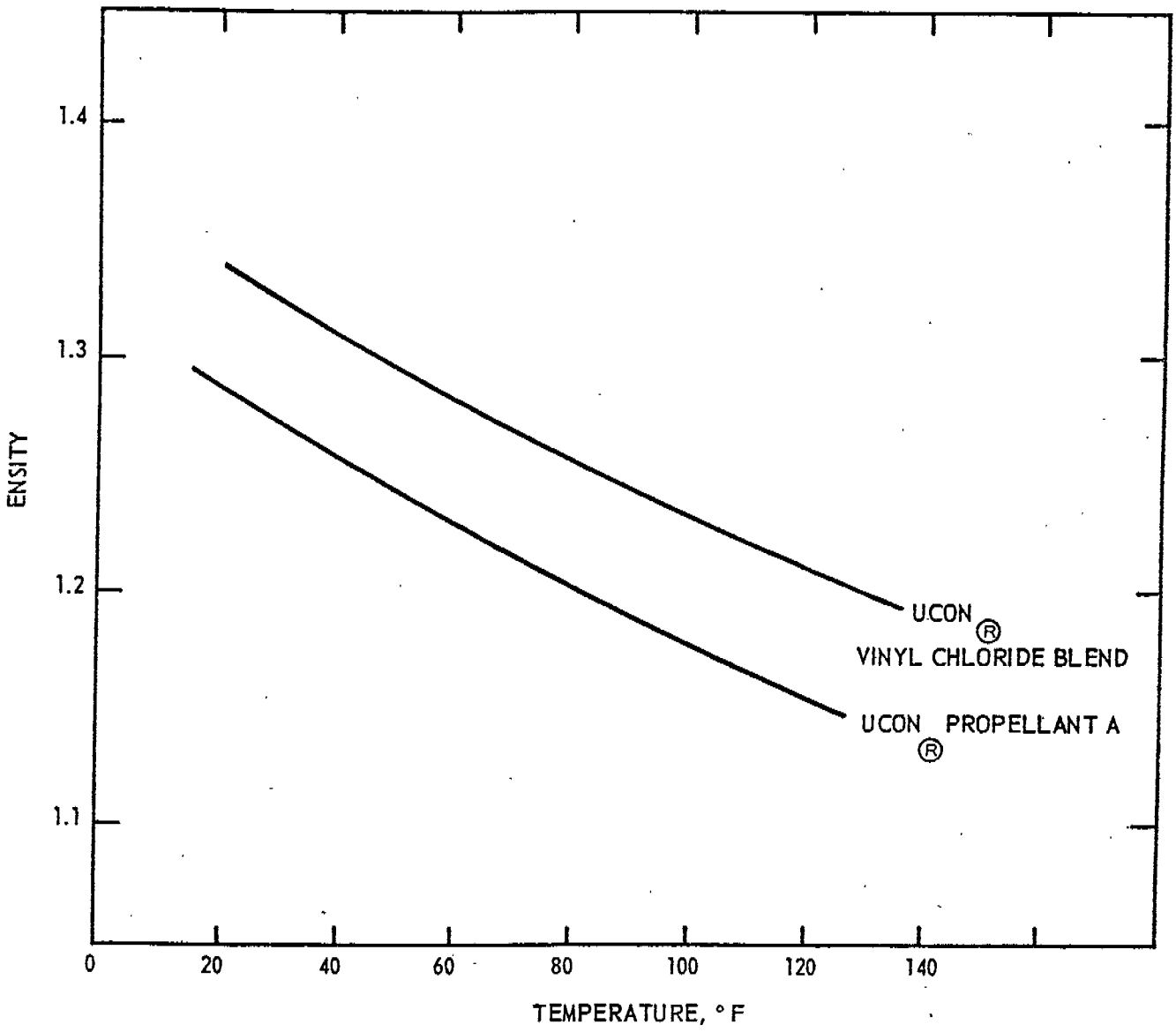
UCON Propellant A and Vinyl Chloride Blend

DENSITY VS. TEMPERATURE

Appendix G

UCON® PROPELLANT A AND VINYL CHLORIDE BLEND

DENSITY VS TEMPERATURE, °F

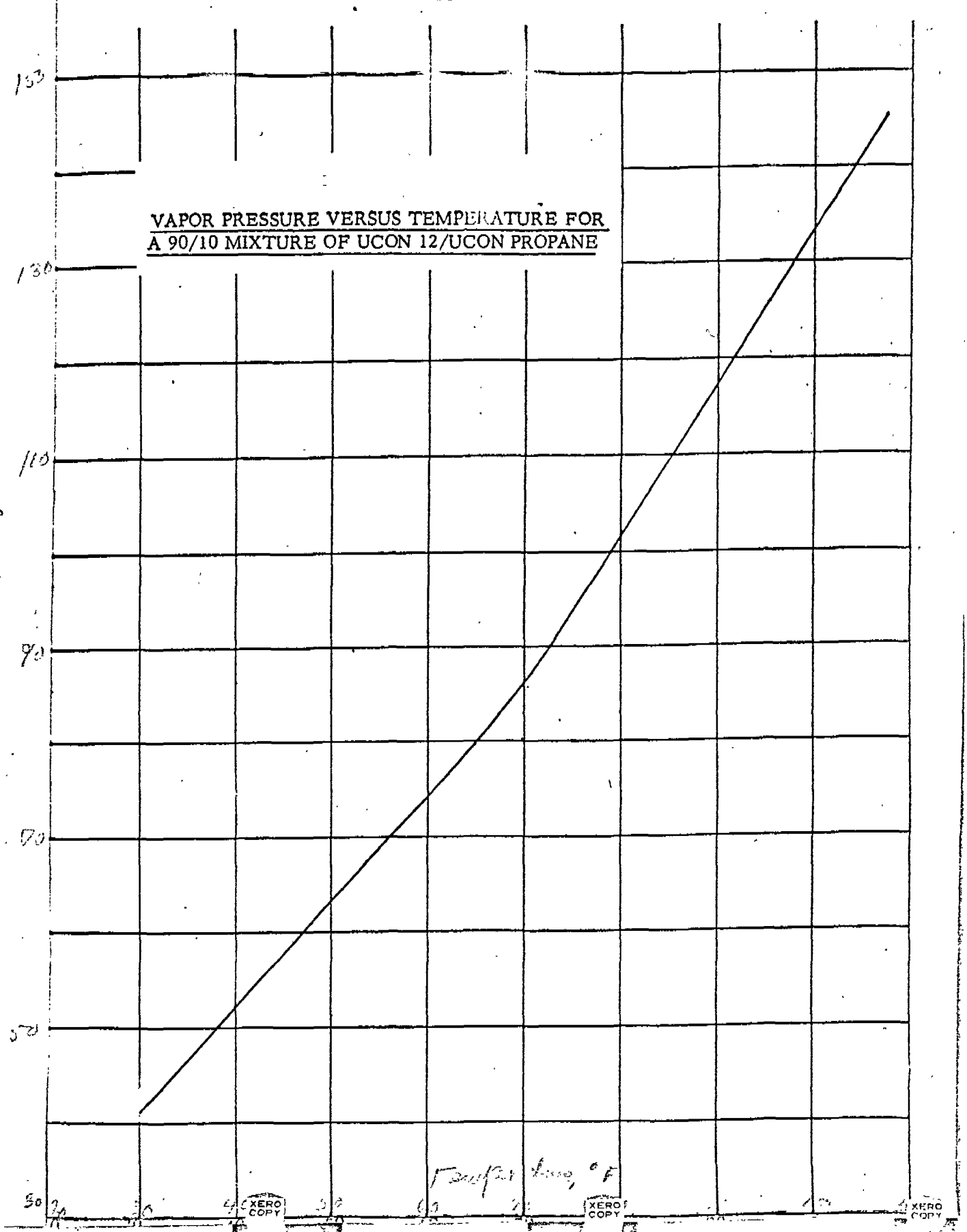


Appendix H

UCON Propellant 12/Propane 90/10

VAPOR PRESSURE VS. TEMPERATURE

Appendix H



Appendix I

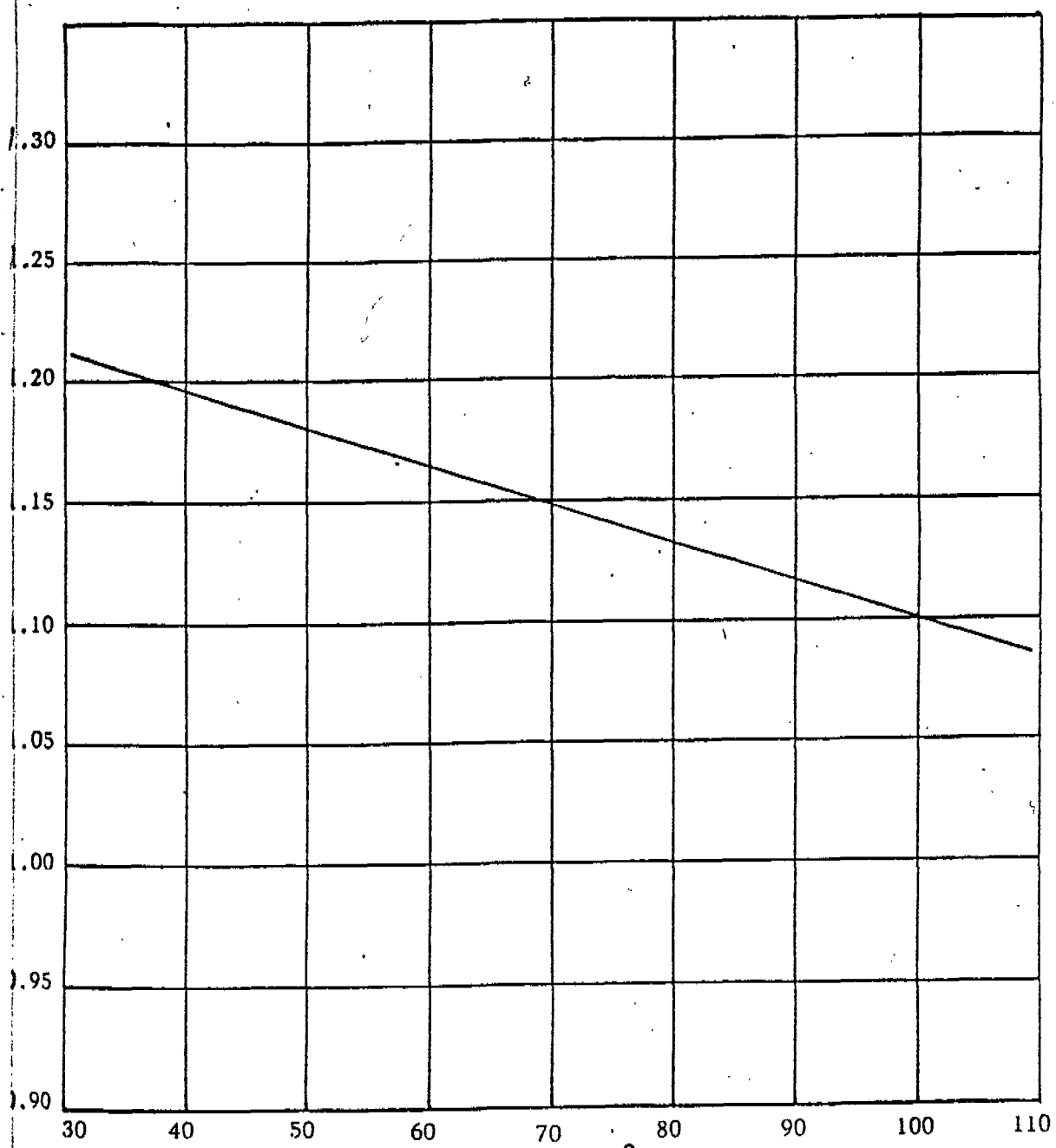
UCON Propellant 12/Propane 90/10

SPECIFIC GRAVITY VS. TEMPERATURE

Appendix I

SPECIFIC GRAVITY VERSUS TEMPERATURE

FOR A 90/10 MIXTURE OF UCON 12/UCON PROPANE



Appendix J

UCON Propellant 12/Isobutane

SPECIFIC GRAVITY VS. COMPOSITION

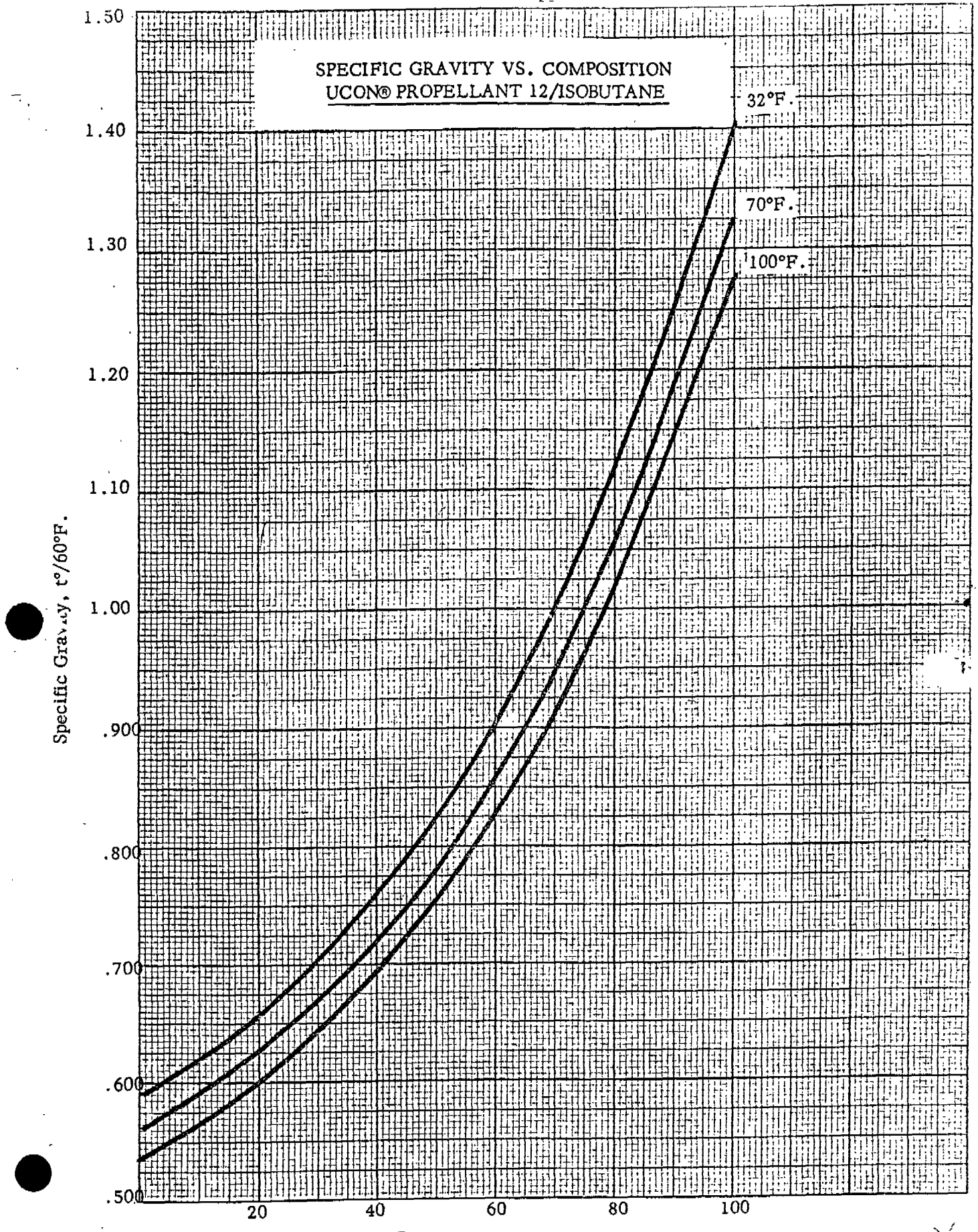


TABLE IV

A REVIEW OF COMPOUNDS TESTED FOR AZEOTROPES WITH FLUOROCARBON 114

Second Component	Results of Study	Remarks *
Vinyl Chloride	Azeotrope discovered	28% Fluorocarbon 114 -14.2°C. Boiling Point
Isobutane	No azeotrope found	
Fluorocarbon 142b	No azeotrope found	
Isobutylene	No azeotrope found	
1-Butene	No azeotrope found	
1,3-Butadiene	Azeotrope discovered	75 - 80% Fluorocarbon 114 -6 to -7°C. Boiling Point
n-Butane	Azeotrope reported previously (8)	59% Fluorocarbon 114 -2.2°C. Boiling Point
cis 2-Butene	No azeotrope found	
trans 2-Butene	Azeotrope discovered	65 - 70% Fluorocarbon 114 -2 to -3°C. Boiling Point
Vinyl Methyl Ether	Azeotrope discovered	60% Fluorocarbon 114 -4.2°C. Boiling Point
Fluorocarbon 133	Azeotrope discovered	63% Fluorocarbon 114 +0.5°C. Boiling Point
Fluorocarbon 21	Azeotrope previously reported (8)	723 mm: 75% Fluorocarbon 114 0.0°C. Boiling Point
Neopentane	No azeotrope found	
Ethyl Chloride	Azeotrope previously reported (7)	83.3% Fluorocarbon 114 1.4°C. Boiling Point
Ethyl Chloride, Fluorocarbon 21	Ternary azeotrope found	83.7% Fluorocarbon 114, 8.5% Ethyl Chloride, 7.8% Fluorocarbon 21 0.8°C. Boiling Point

* Compositions are in weight %.

TABLE V

PROPERTIES OF FLUOROCARBON 114 AZEOTROPES

Azeotrope	Toxicity	Flammability	Remarks
Vinyl Chloride	Low	Flammable	
1,3-Butadiene	Low	Probably Flammable	Possesses bad odor, butadiene will polymerize
n-Butane	Low	Flammable	
t-2-Butene	None	Probably Flammable	Possesses bad odor
Methyl Bromide	Very high	Probably Flammable	
Vinyl Methyl Ether	Low	Not Known	May polymerize
Fluorocarbon 133	None	Nonflammable	
Fluorocarbon 21	None	Nonflammable	Hydrolysis of Fluorocarbon 21 would be problem in aqueous system
Ethyl Chloride	None	Nonflammable	
Fluorocarbon 21, ethyl chloride	None		Hydrolysis may occur in aqueous systems

D. Ternary Systems

It is possible to extend all the concepts presented above to a system in which three components comprise the mixture of interest. The existence of ternary azeotropes is well known and these are almost always found to be of the minimum boiling type. It was, therefore, decided to investigate certain specially selected fluorocarbon systems for ternary azeotropes.

Because such a large number of possible ternary combinations can be conceived, it was necessary to use a set of selection rules. These are listed below:

1. At least two binary azeotropes should exist between the three components if a ternary azeotrope is to be expected.
2. No compounds of high reactivity, toxicity, or cost were considered.
3. The composition of the azeotrope was estimated by plotting the system on a ternary diagram and drawing dilution lines from the known binary azeotropic compositions toward the opposite apices. The point of intersection of the dilution lines indicates the area in which an azeotrope is most likely to be found if one were to exist in the system. If one of the components is flammable and the flammability curve is known, it should also be possible to assess the flammability of the mixture from the predicted compositions.

The method described in Item 3 is applied to some systems of interest in Figure 6, where fluorocarbons 21 and 114 represent the lower apices of a ternary diagram, and third components are shown at the top. Consider,

for example, the n-butane/fluorocarbon 114/21 system. The two binary azeotropes: butane/fluorocarbon 114 80.5/19.5 and fluorocarbon 21/114 35.7/64.3 (ratios in mole per cent) are plotted on the corresponding sides of the diagram and dilution lines are drawn to the opposite apices. The two dilution lines cross at the point where the composition of the system in mole per cent is 57% butane, 28% flurocarbon 114, and 15% fluorocarbon 21. This value is found to be in fair agreement with the azeotropic composition determined: 57.8% butane, 33.2% fluorocarbon 114, and 9.6% fluorocarbon 21.

(Figure 6)

If one applies the selection rules to fluorocarbon 12 systems, the following binaries are of interest:

Fluorocarbon 22/Fluorocarbon 12

Fluorocarbon 152a/Fluorocarbon 12

Dimethyl ether/Fluorocarbon 12

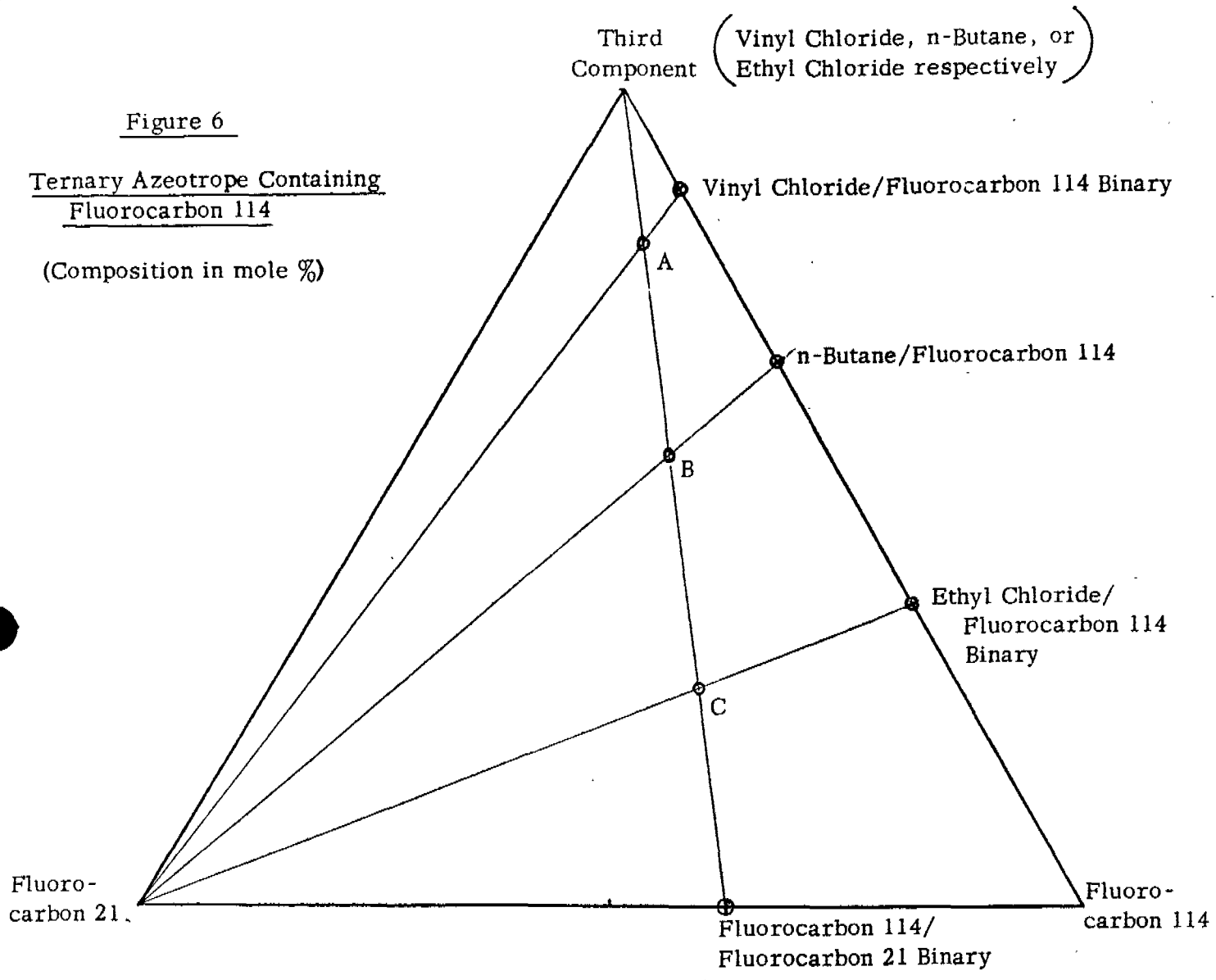
Any azeotrope with fluorocarbon 22 would have too high a pressure to be of much value as a propellant, and it was found that no ternary azeotrope exists in the systems: fluorocarbon 12/22/152a and fluorocarbon 12/22/dimethyl ether.

The ternary systems which offer the most promise would be those involving fluorocarbon 114, since so many binaries are known. The binaries used to construct three-component systems are listed below:

Figure 6

Ternary Azeotrope Containing Fluorocarbon 114

(Composition in mole %)



Predicted Ternary Azeotropes

A	B	C
83% Vinyl Chloride	57% n-Butane	26% Ethyl Chloride
12% Fluorocarbon 114	28% Fluorocarbon 114	48% Fluorocarbon 114
6% Fluorocarbon 21	15% Fluorocarbon 21	36% Fluorocarbon 21

Fluorocarbon 114/n-Butane

Fluorocarbon 114/Ethyl Chloride

Fluorocarbon 114/Vinyl Chloride

Fluorocarbon 114/Fluorocarbon 21

Some of these binary azeotropes are flammable by themselves; however, it was thought that ternary systems might be found which would be nonflammable by virtue of dilution of the flammable component. In the case of binary azeotropes that were nonflammable, it was anticipated that more of the flammable components might be incorporated into the ternary mixtures. The prediction of the composition of the possible ternary systems is shown in Figure 6, where the fluorocarbon 114/21 binary is held constant and the other three binaries are plotted against it. Thus, in the vinyl chloride/fluorocarbon 114 and 21 system, the point of intersection of the dilution line for the vinyl chloride/fluorocarbon 114 binary and the fluorocarbon 114/21 binary represents the predicted composition for the ternary azeotrope. In this case the system was eliminated from consideration since the predicted composition was far above the maximum allowable level of vinyl chloride established by previous measurements[2] and would,therefore, be flammable. Similarly, the n-butane, fluorocarbon 114 and fluorocarbon 21 system, which was discussed above, would be flammable according to the flammability curve[3]. The ethyl chloride/-fluorocarbon 114/21 system was investigated, and a ternary azeotrope was discovered with a mole ratio of 19/70/11. This differed considerably from the predicted composition of 26/48/36. The system could be of value as a propellant for colognes and perfumes, since it is nonflammable and is economically attractive.

SUMMARY

In an effort to discover useful fluorocarbon azeotropes, a study of a large number of systems was undertaken. The methods of ebulliometry and distillation were used to detect azeotropes. Some new azeotropic mixtures were discovered; however, only a limited number possessed those properties necessary for a safe and effective aerosol propellant. In particular, the binary mixture ethyl chloride/fluorocarbon 114 with a weight ratio of 16.7/83.3 and the ternary ethyl chloride/fluorocarbon 114/21 with a weight ratio of 8.5/83.7/7.8 appear to be suitable for low-pressure applications.

EXPERIMENTAL

A. Ebulliometer[9]

The instrument was constructed from a Cotrell-type molecular weight apparatus that was vacuum-jacketed and fitted with a thermocouple and a system for circulating methanol cooled by dry ice through the condenser section. Materials were added through the condenser from standard aerosol cans which could be fitted with "tap-a-can" valves and weighed after each addition. The level of liquid in the instrument could be controlled by withdrawing liquid from the sample tube in measured amounts. The condenser section was designed in such a way that the rate of reflux could be observed and the amount of heat applied by the mantle could be controlled accordingly.

B. Distillation

A Podbielniak fractional distillation column #80 was used. This instrument was entirely vacuum-jacketed and fitted with a solenoid release to control the reflux rate. Thermocouples placed in the head of the column, the still pot, and the methanol dry ice cooling system were connected to a recorder which monitored all three temperatures. Samples were collected as liquids.

C. Gas Chromatograph

Analysis of distillation fractions was performed on an Aerograph A-90-P instrument. Known mixtures of the components were used in each case to calibrate the instrument before distillation fractions were analyzed.

Ternary systems were investigated by distillation-gas chromatography.

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Appendix N

A BASIC SYSTEM FOR WATER-BASED PRODUCTS

By

R. J. Scott and M. E. Clayton

Union Carbide Corporation

Chemicals Division

Technical Service Division

Tarrytown, New York

INTRODUCTION

Water-based aerosol products are not new; some of them, such as cleaners and polishes, have been on the market for many years. These products are usually in the form of oil-in-water (O/W) emulsions with the propellant dissolved in the oil phase. Upon ejection, this system produces a coarse, wet spray because the propellant is present in low concentration and the propellant-oil droplets are surrounded by water. Such sprays, however, are quite satisfactory for residual-type products where the primary function is merely to deposit a material on a surface.

Water-based space sprays are quite different from the residual type and have become a major factor in the aerosol field. This paper presents the results of a study on water-based space sprays that was carried out in the UCON® Refrigerants and Propellants Laboratory. The system that evolved was not adapted to specific products but is offered as a starting point for those interested in developing aqueous products that require relatively fine sprays.

DISCUSSION

There are at least three systems that can be used for water-based space sprays:

1. A true solution of propellant and aqueous concentrate,
2. A three-phase system with the propellant forming a separate floating layer, and
3. An emulsion of the propellant and concentrate.

The first has already been described in the literature* and the second is disclosed in U. S. Patent 2,995,278, assigned to Mr. Clarence Clapp. The third seems to be receiving the most attention in the industry today and is the one that will be discussed in this paper.

It was apparent at the outset that a water-in-oil (W/O) emulsion of propellant and aqueous concentrate would have two advantages: (1) It would produce a finer spray than an O/W emulsion since the propellant can more readily escape and, (2) contact of the container surface and oil-soluble active components with water is limited--since water forms the internal phase, it has less opportunity to hydrolyze active components in the oil phase or to contact the container walls. Therefore, it was decided to work with W/O emulsions as the basis for the system.

It was also recognized that a mixture of a fluorocarbon and a hydrocarbon would have advantages over a hydrocarbon alone as the propellant. In particular, the density of the propellant phase would be increased which, in turn, should increase the emulsion stability. Since the vapor pressure of isobutane falls in the range of moderate-pressure propellants, it was chosen as the hydrocarbon portion of the propellant mixture. Propellant 12 was chosen as the fluorocarbon because of its resistance to hydrolysis; although Propellant 11 is reportedly being used with aqueous systems, it was not included in the present work because of its hydrolytic susceptibility. The particular fluorocarbon-to-hydrocarbon ratio that could be used was governed by the ICC pressure limitation of 40 psig at

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*D. C. Geary, "Low-Cost Water-Based Aerosols", Soap and Chemical Specialties, 36, No. 3, 135 (1960).

70°F., since the pressure in the containers will be the vapor pressure of the propellant itself. A Raoult's Law calculation shows that a 30/70 mixture of propellant 12 and isobutane should have a vapor pressure of 36 psig at 70°F.; experimentally the pressure was found to be about 40 psig. Thus, the 30/70 ratio represents about the maximum amount of propellant 12 that can be incorporated and still remain under the pressure limit for sideseam containers. The density of this mixture is increased significantly over that of the hydrocarbon, as can be seen in Figure 1, where the specific gravity vs. composition is shown for all mixtures of Propellant 12 and isobutane.

(Figure 1)

The final item that had to be considered before starting experimental work was the propellant/concentrate ratio. This was somewaht arbitrarily set at 35/65 in the beginning, but was subsequently changed toward larger propellant concentrations as the work progressed.

Having selected the propellants and their concentration, an experimental evaluation of surfactants was begun. Use was made of the HLB system to facilitate rapid screening of a large number of surfactants. The lower th HLB number, the more lipophilic is the surfactant and the greater the tendency for it to form W/O emulsions. Therefore, the surfactants and their combinations were chosen so that those with low HLB numbers predominated.

In all, a total a twenty-four surfactants or surfactant mixtures were tested with a simple 35 per cent propellant - 65 per cent water combination.

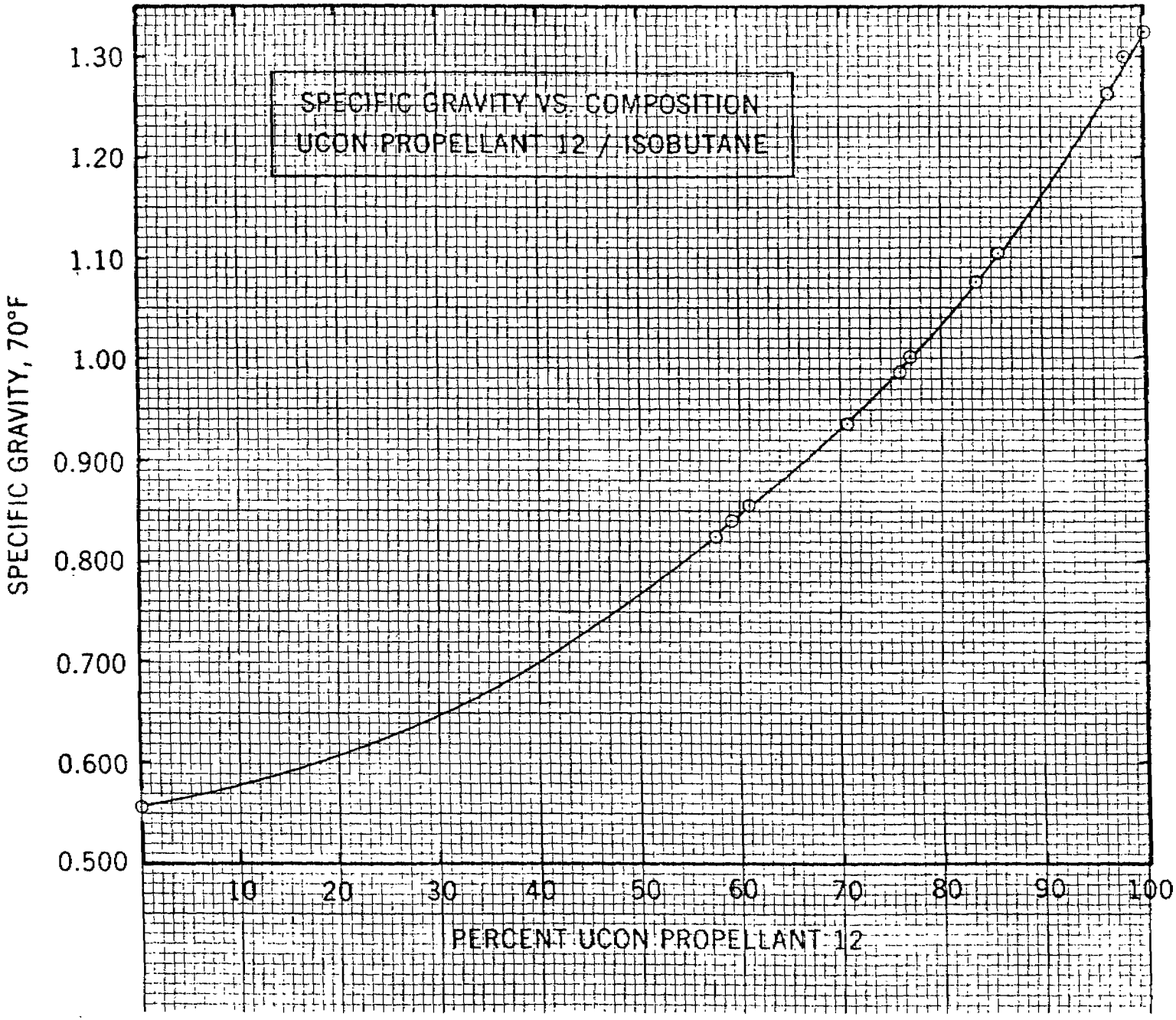

SPECIFIC GRAVITY VS. COMPOSITION
UCON PROPELLANT 12 / ISOBUTANE
SPECIFIC GRAVITY, 70°F
1.30
1.20
1.10
1.00
0.900
0.800
0.700
0.600
0.500
10
20
30
40
50
60
70
80
90
100
PERCENT UCON PROPELLANT 12

Figure 1.

Varying degrees of emulsion stability were obtained, but in no case was an acceptable spray produced. It was evident that a different approach would be required.

It was expected that the addition of a cosolvent that was soluble in both the propellant and water would improve the stability of the emulsions and the type of spray that was ejected. The cosolvents that were tried and the formulation changes that were made are listed in the Table. Cosolvents such as isopropanol and hexylene, triethylene, and dipropylene glycols generally improved emulsion stability but not the quality of the spray. A mineral oil (Shell Sol 71), however, produced "transparent" emulsions with fine, colorless and quite satisfactory sprays (mixtures 10 and 11 in Table I). Strictly speaking, the mineral oil was not a cosolvent for the propellant and water but probably served more as a carrier for the surfactant, and may have altered the HLB of the nonaqueous phase. Other mineral oils would probably perform as well.

(Table I)

TABLE I

W/O EMULSION FORMULATIONS CONTAINING COSOLVENTS

	Formulation	Observations
1.	50% Water, 7% Hexylene Glycol, 1% Emcol 14, 7% Shell Sol 71, 35% UCON 12/Isobutane (30/70)	Very foamy, opaque, white emulsion. Snow-like spray.
2.	50% Water, 14% Hexylene Glycol, 1% Emcol 14, 35% UCON 12/Isobutane (30/70)	Separates on standing, easily reemulsified. Fair spray.
3.	50% Water, 14% Isopropanol, 1% Emcol 14, 35% UCON 12/Isobutane (30/70)	About the same as #2; slightly finer spray.
4.	50% Water, 1% Emcol 14, 14% Shell Sol 71, 35% UCON 12/Isobutane (30/70)	Grayish, opaque emulsion. Fairly good spray.
5.	45% Water, 4.5% Hexylene Glycol, 1% Emcol 14, 4.5% Shell Sol 71, 45% UCON 12/Isobutane (30/70)	Grayish-white, opaque emulsion. Foamy spray.
6.	40% Water, 14% Hexylene Glycol, 1% Emcol 14, 45% UCON 12/Isobutane (30/70)	Opaque, white emulsion. Poor spray.
7.	49% Water, 1% Emcol 14, 50% UCON 12/ Isobutane (30/70)	Grayish-white, opaque emulsion. Tends to foam at button.
8.	53% Water, 10% Triethylene Glycol, 1.8% Span 80, 0.2% Tween 85, 35% UCON 12/Isobutane (30/70)	Emulsion separates quickly. Poor spray.
9.	54% Water, 10% Dipropylene Glycol, 1% Emcol 14, 35% UCON 12/Isobutane (30/70)	Thick white emulsion, separates slowly. Poor spray.
10.	44% Water, 1% Emcol 14, 10% Shell Sol 71, 45% UCON 12/Isobutane (30/70)	Translucent appearance in container. Very fine, almost colorless spray.
11.	46% Water, 1% Emcol 14, 5% Shell Sol 71, 48% UCON 12/Isobutane (25/75)	Grayish emulsion. Very fine, almost colorless spray.

The last two mixtures in the Table are summarized below as recommended starting points f r the development of water-based space spray products:

Component	Concentration, % by Weight	
	I	II
Shell Sol 71	10%	5%
Emcol 14	1%	1%
Water	44%	46%
UCON Propellant 12/Isobutane 30/70	45%	--
UCON Propellant 12/Isobutane 25/75	--	48%

The reason for the two propellant ratios is the pressure limitation of 40 psig at 70°F. The 10 per cent oil in the first mixture lowers the pressure well below 40 psig, but with only 5 per cent oil in the second mixture, it was deemed advisable to alter the propellant composition. As far as the spray qualities are concerned, there is not much difference between the two.

Appendix O

EQUIPMENT SUPPLIERS

EQUIPMENT SUPPLIERS

Actuator Button-Placers

Haumiller Engineering Co.

PMC Industries, Inc.

Ball-Feeders

J. G. Machine Works, Inc.

Bottle-Testers

J. G. Machine Works, Inc.

Bottle-Crimpers

J. G. Machine Works, Inc.

Can-Unscramblers

Horix Manufacturing Co.

Island Equipment Corp.

J. G. Machine Works, Inc.

MRM Co., Inc.

Pneumatic Scale Corp., Ltd.

Cappers

Consolidated Packaging Mach. Corp.

Pneumatic Scale Corp. Ltd.

Resina

Case-Packers

Burt Machine Co.

Chisholm-Ryder Co. of Pa.

Miller-Hydro Co.

Standard-Knapp Div., Emhart Mfg. Co.

Case-Sealers

Chisholm-Ryder Co. of Pa.

Elliott Mfg. Co.

Standard-Knapp Div., Emhart Mfg. Co.

Textile Machine Works

Container-Cleaners

Chisholm-Ryder Co., of Pa.

Island Equipment Corp.

Machinery Service Co.

MRM Co., Inc.

Standard-Knapp Div., Emhart Mfg. Co.

Coders

Adolph Gottscho, Inc.

Industrial Marking Equipment Co., Inc.

Kiwi Coders Corp.

Standard-Knapp Div., Emhart Mfg. Co.

Conveyors

Island Equipment Corp.

Leeds Conveyor Mfg. Co.

Crimpers

Consolidated Packaging Mach. Corp.

Kartridg Pak Co., The

Nalbach, John R., Engineering Co., Inc.

J. G. Machine Works, Inc.

Drive Units

J. G. Machine Works, Inc.

Labelers

Burt Machine Co.

Chisholm-Ryder Co., of Pa.

MRM Co., Inc.

New Jersey Machine Corp.

Standard-Knapp Div., Emhart Mfg. Co.

Liquid Fillers

Colton, Arthur, Co.,
Div. of Snyder Corp.

Elgin Manufacturing Co.

Horix Manufacturing Co.

Kiefer, Karl, Machine Co., The

MRM Co., Inc.

Nalbach, John R., Engineering,
Co., Inc.

Product Fillers

J. G. Machine Works Inc.

Propellant Accumulators

J. G. Machine Works, Inc.

Propellant Fillers

Economic Machiner Co., Div.
of George J. Meyer Mfg. Co.

Kartridge Pak. Co, The

Kiefer, Karl, Machine Co., The

Propellant Reclaimers

J. G. Machine Works, Inc.

Pumps

J. G. Machine Works, Inc.

Purgers

J. G. Machine Works, Inc.

Test Tanks

Island Equipment Corp.

Nalbach, John R., Engineering
Co., Inc.

Valve-Inserters

Consolidated Packaging Mach. Corp.

Machinery Systems Inc.

PMC Industries, Inc.

Burt Machine Co.
410-03 E. Barclay St.
Baltimore 2, Md.

Chisholm-Ryder Co. of Pennsylvania
Hanover, Pa.

Colton, Arthur, Co.
Div. of Snyder Corp.
3400 E. Lafayette Ave.
Detroit 7, Michigan

Consolidated Packaging Machinery Corp.
Subs. of International Paper Co.
1400 West Ave.
Buffalo 13, N. Y.

Economic Machinery Co.
Div. of George J. Meyer Mfg. Co.
60 Fremont St.
Worcester 3, Mass.

Elgin Manufacturing Co.
P. O. Box 73
Elgin, Ill.

Elliott Manufacturing Co.
P. O. Box 469
Fresno 1, Calif.

Adolph Gottsch, Inc.
6 Evans Terminal
Hillside, N. J.

Haumiller Engineering Co.,
Elgin, Illinois

Horix Manufacturing Co.
P. O. Box 9324
Pittsburgh, Pa.

Industrial Marking Equipment Co., Inc.
655 Berriman St.
Brooklyn 8, N. Y.

Island Equipment Corp.
P. O. Box 38-279
Miami 38, Fla.

J. G. Machine Works, Inc.
14-20 Poplar Ave.
Little Ferry, New Jersey

Kartridg Pak Co., The
800 W. Central Rd.
Mt. Prospect, Illinois

Kiefer, Karl, Machine Co., The
Div. of Cherry-Burrell Corp.
937 Martin St.
Cincinnati 2, Ohio

Kiwi Coders Corp.
4027 N. Kedzie Ave.
Chicago 18, Illinois

Leeds Conveyor Manufacturing Co.
East Haven, Connecticut

MRM Co., Inc.
E. Beth Page Road
Plainview, Long Island, N. Y.

Machinery Service Co.
P. O. Box 14067
Louisville 14, Ky.

Machinery-Systems, Inc.
2800 Sisson St.
Baltimore 11, Md.

Miller-Hydro Co.
Bainbridge, Ga.

Nalbach, John R., Engineering Co., Inc.
6139 W. Ogden Ave.
Chicago 50, Ill.

New Jersey Machine Corp.
1500 Willow Avenue
Hoboken, N. J.

PMC Industries
293 Hudson St.
Hackensack, N. J.

Pneumatic Scale Corp. Ltd.
77 Newport Ave.
Quincy 71, Mass.

Resina
572 Smith Street
Brooklyn 31, N. Y.

Standard-Knapp Division
Emhart Mfg. Co.,
Portland, Conn.

Textile Machine Works
Packomatic Div.
P. O. Box 1382
Reading, Penna.

Appendix K

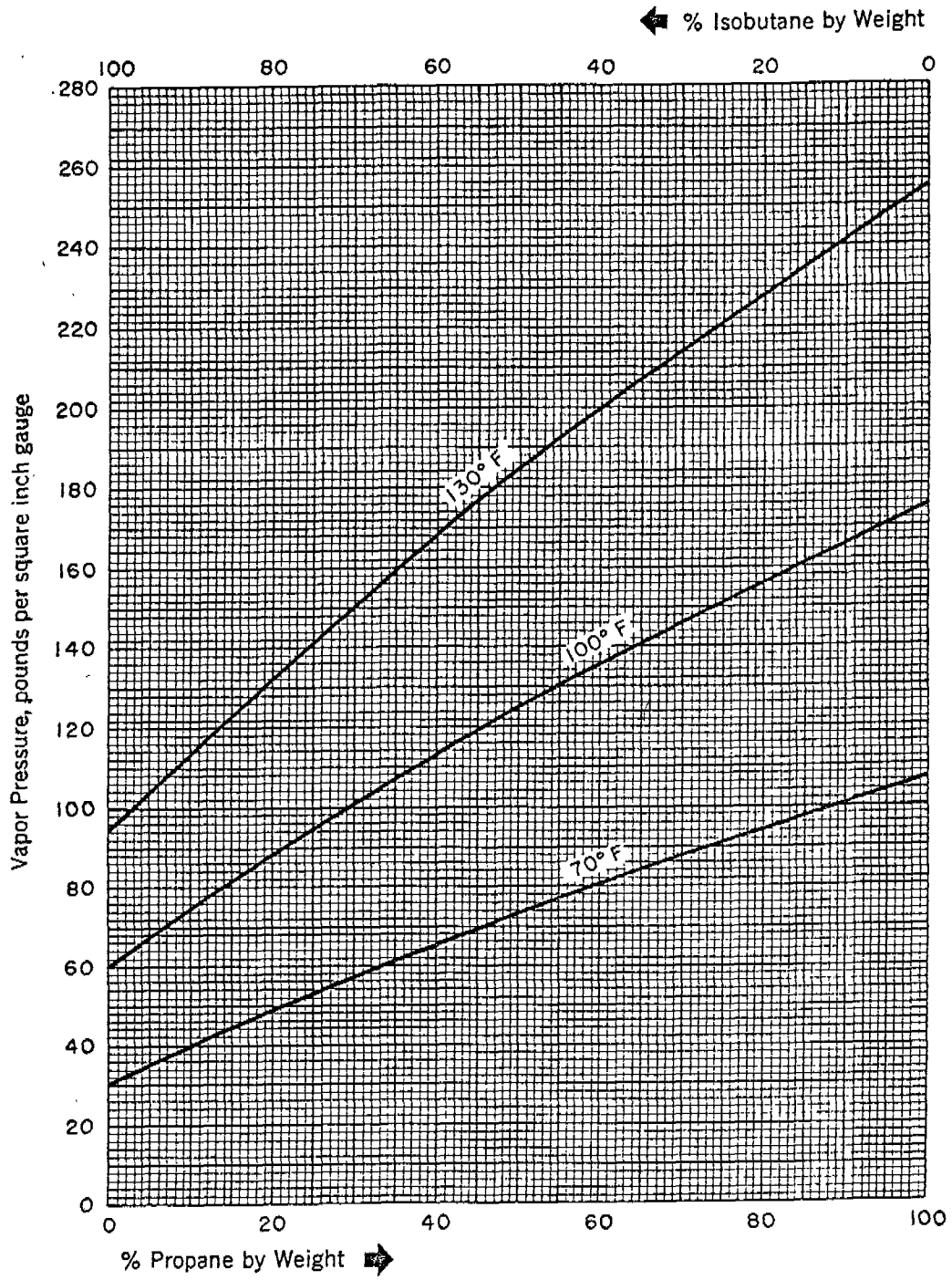
UCON Propane/Isobutane Blends

VAPOR PRESSURE VS. COMPOSITION

Appendix K

VAPOR PRESSURE VS. COMPOSITION

UCON Isobutane–Propane Blends



Appendix L

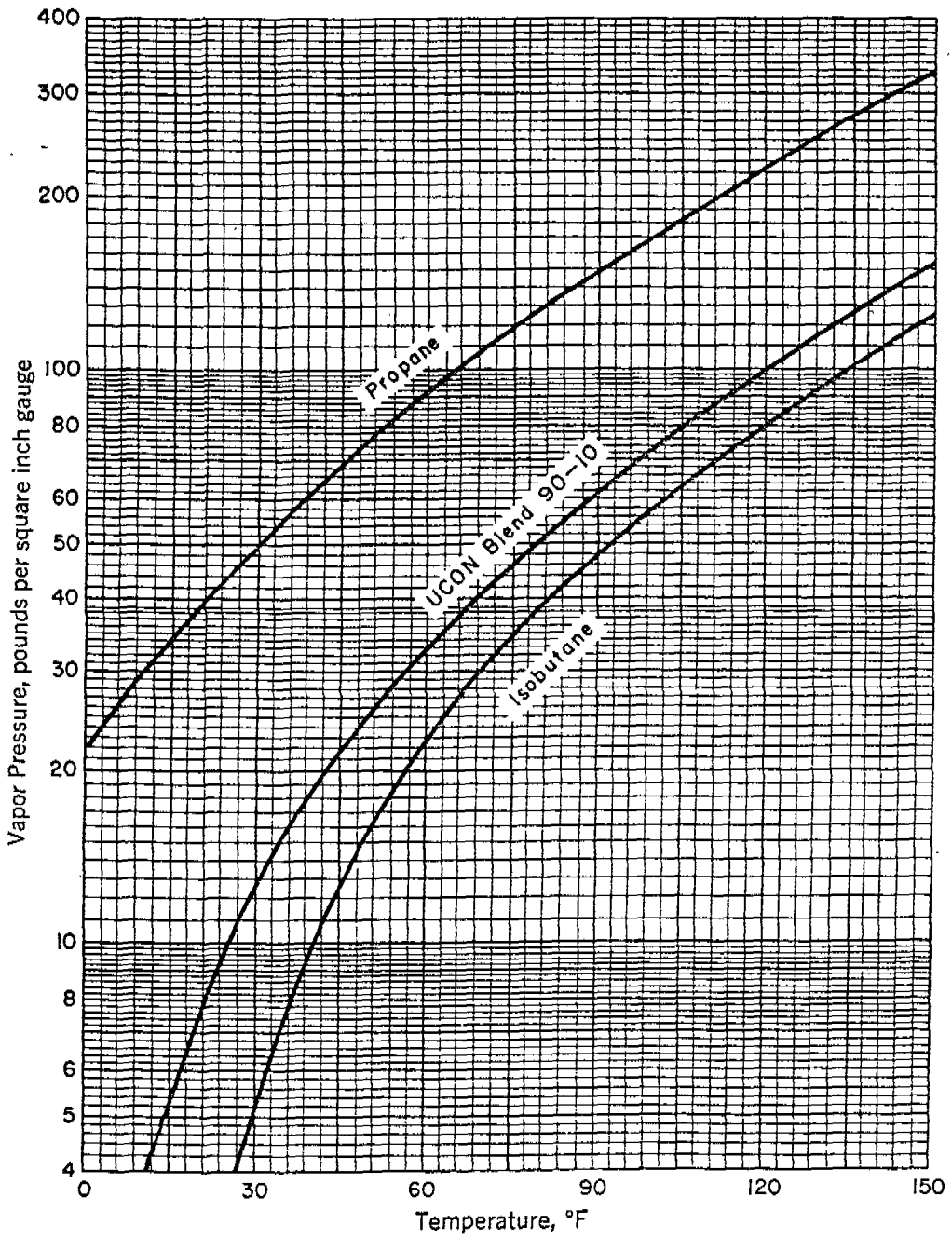
UCON Hydrocarbon Propellants

VAPOR PRESSURE VS. TEMPERATURE

Appendix L

VAPOR PRESSURE VS. TEMPERATURE

UCON Hydrocarbon Propellants



Appendix M

AZEOTROPIC AEROSOL PROPELLANTS

By

J. R. Haase and R. J. Scott

Union Carbide Corporation

Chemicals Division

Technical Service Laboratory

Tarrytown, New York

INTRODUCTION

Azeotropes have two unique properties that make them attractive as potential aerosol propellants. First, under evaporative conditions, an azeotrope functions as a single entity and does not fractionate. In the case of aerosol propellant blends, fractionation was a common characteristic[1-5], and some of their economic advantage had to be sacrificed to avoid the hazards which it caused.

The second useful property of azeotropes is their vapor pressure; i. e., most azeotropes have vapor pressures higher than those of the individual components. In the case of propellants 11 and 114, for example, propellant 12 is often added to provide sufficient pressure for a given application. Azeotropes of propellant 11 or 114 with other compounds could have vapor pressures sufficiently high to reduce the need for propellant 12, or reduce the total propellant requirement in a product.

Considering the potential value of azeotropic systems as aerosol propellants and the fact that several systems involving fluorocarbons were known[6,7,8], it was apparent that a definitive investigation of fluorocarbon azeotropes would be of considerable interest. Such a study was carried out in the UCON® refrigerants and propellants laboratory. It should be noted that, although this paper is concerned primarily with aerosol propellants, any of the mixtures discussed below that possess the requisite properties would be equally suitable as refrigerants.

DISCUSSION

A. What is an Azeotrope?

The relationship between the vapor pressure and concentration of components in an ideal solution is given by Raoult's Law:

$$P_A = x_A P_A^{\circ}$$

where: P_A = The vapor pressure of component A in the mixture.

x_A = The mole fraction of component A in the mixture.

P_A° = The vapor pressure of pure component A under the given conditions.

The total vapor pressure of a system can be expressed as the summation of the Raoult's Law expressions for each component:

$$P = P_A + P_B + \ldots + P_n$$

These relationships are represented graphically by the broken lines in Figure 1.

In practice this relationship is very seldom observed except in the regions where x_A approaches zero or one. Real systems give curves resembling the solid lines in Figure 1, with either higher vapor pressures than predicted (positive deviations) or lower vapor pressures than predicted (negative deviations). The magnitude of these deviations from ideality varies over a wide range. They may extend to a point where the total pressure of the system reaches a maximum value above that of either pure component. The vapor pressure - composition curve for a system with extensive positive * deviation is shown in Figure 2. Figure 3 (which has

* Our discussions will pertain to systems with positive deviations, since these are by far the most common.

an inverse relationship to Figure 2) shows the boiling point - composition curve for the same system. Temperature - composition curves for liquid and vapor are shown in Figure 4, where it can be seen that, at the niminum, the composition is the same for both phases. Thus, liquid mixtures for which this relationship holds (ones in which the liquid and vapor have the same composition at equilibrium) are called azeotropes.

(Figure 1)

(Figure 2)

(Figure 3)

(Figure 4)

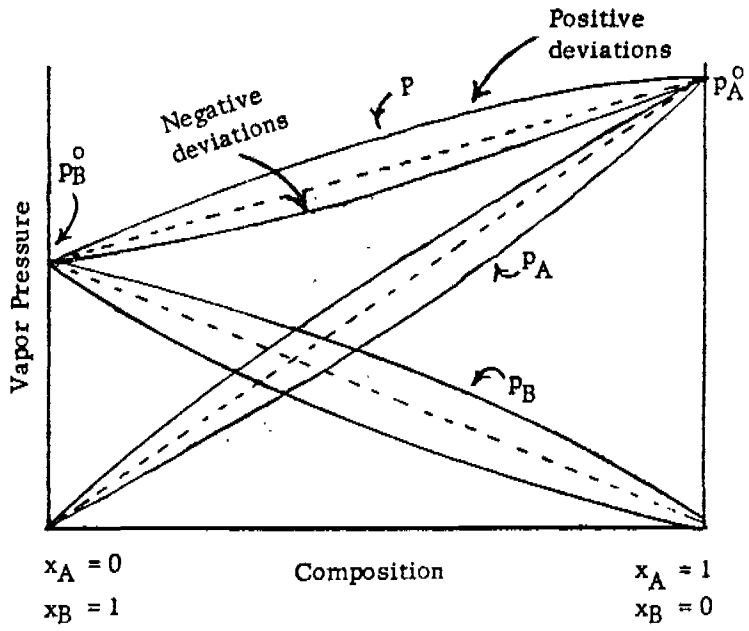


Figure 1

Vapor Pressure-Composition Curves for Ideal and Nonideal Systems

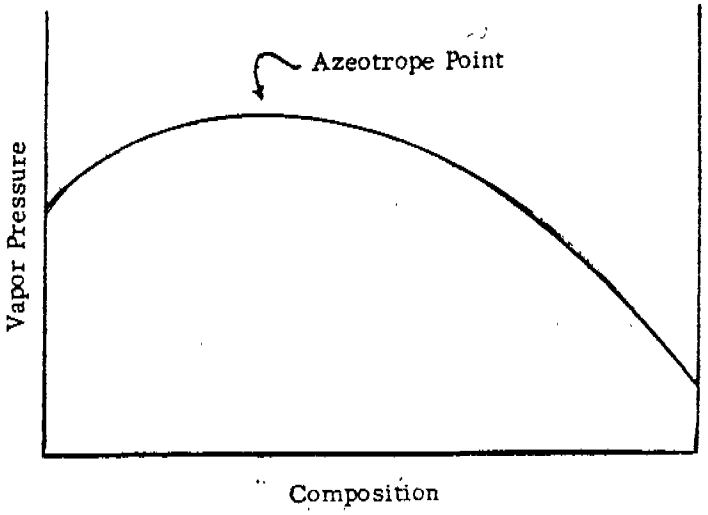


Figure 2

Vapor Pressure-Composition Curve for a System with Extensive Deviations from Raoult's Law

Figure 3

Boiling Point-Composition Curve for a System with Extensive Deviations from Raoult's Law

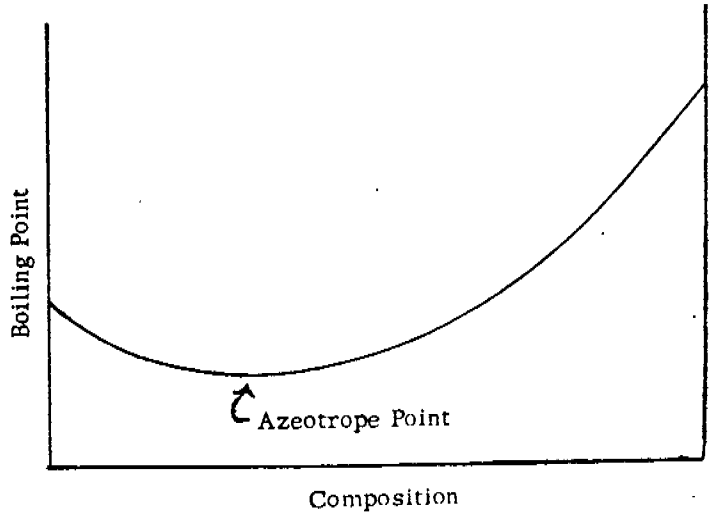
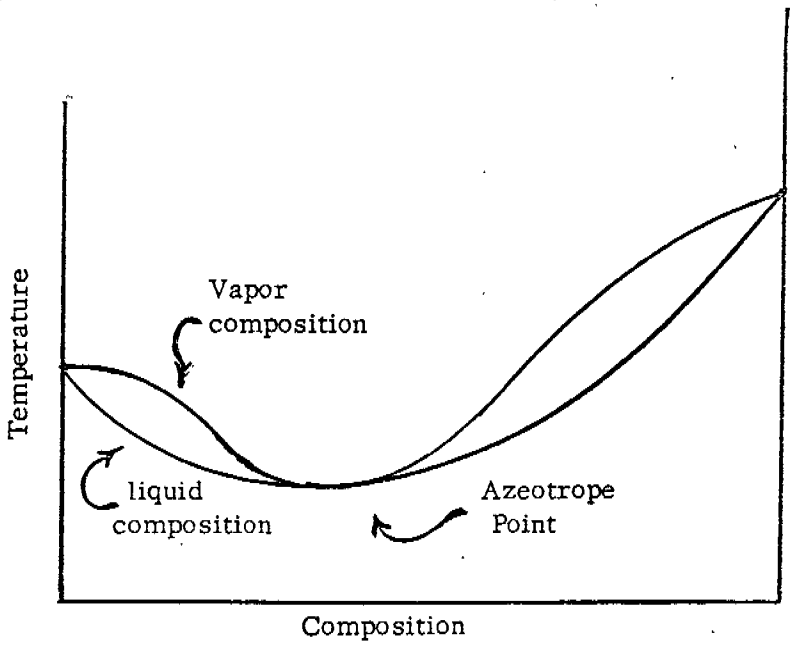


Figure 4

Vapor Liquid Equilibrium Curve for Azeotropic System

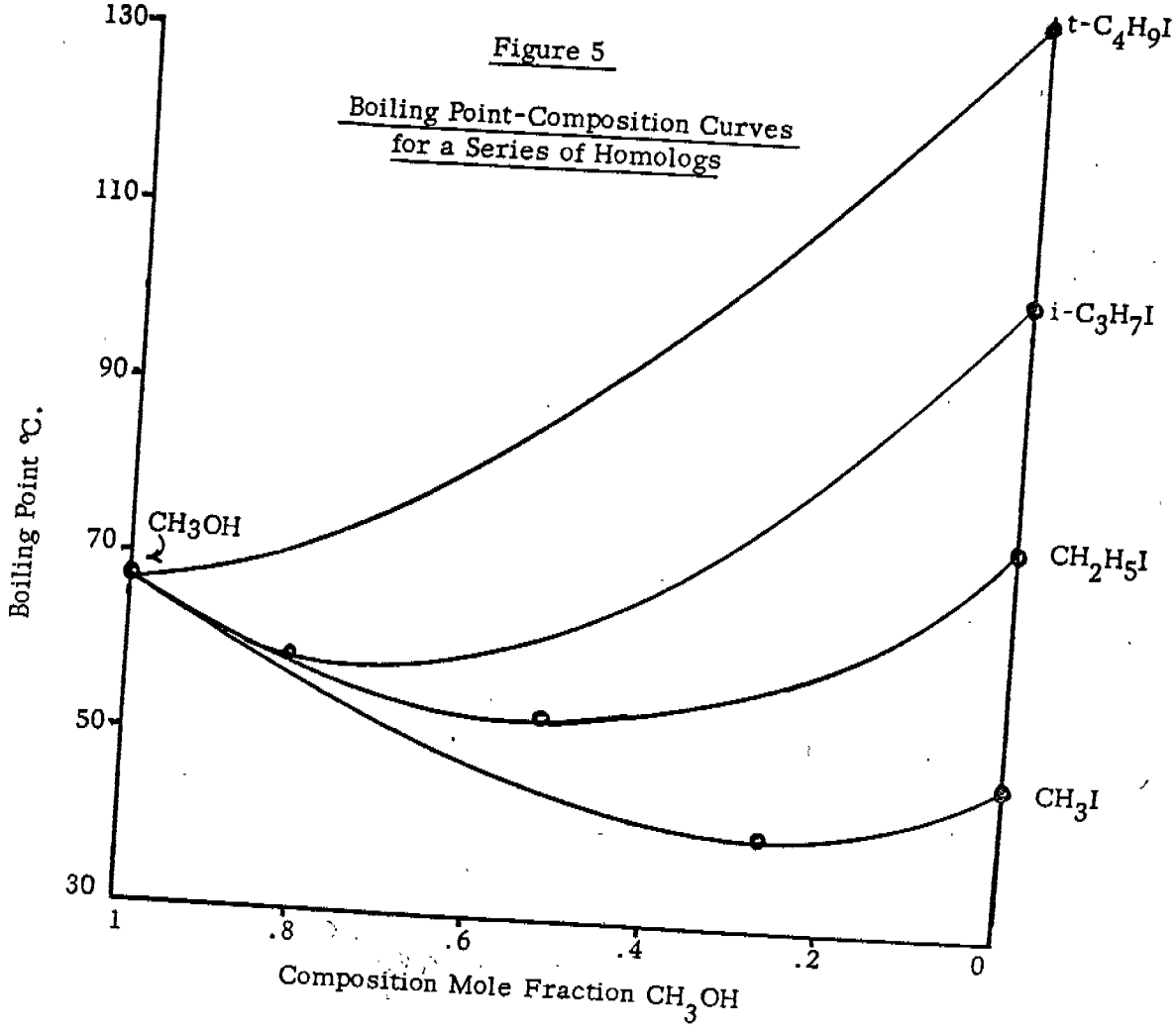


The magnitude of deviations from Raoult's Law must also be considered in relation to the boiling point separation of the pure components involved. Figure 5 shows a series of boiling-point curves in which one component is kept constant while the second component is varied over a series of homologs. As can be seen from Figure 5, when the boiling points are close together the azeotrope is rich in both components (e. g. Methanol/Ethyl Iodide system). If the boiling points are far apart, the azeotrope should contain more of one component than another (e. g. Methanol/Isopropyl Iodide system and Methanol/Methyl Iodide system). Further, when the boiling points are separated by a large amount relative to the extent of the deviations from Raoult's Law, azeotropic activity may disappear altogether (e. g. Methanol/ tert-Butyl Iodide system). Thus, the formation of azeotropes is related to both the boiling point and chemical structure of the two components. These considerations are useful in selecting systems for investigation when, for example, a fluorocarbon is the fixed component and the homologs are flammable. In order that the resulting mixture be nonflammable, it may be necessary to have a low concentration of the homolog, and one would look for candidates with boiling points significantly higher than that of the fluorocarbon.

(Figure 5)

Figure 5

Boiling Point-Composition Curves for a Series of Homologs



B. Detecting Azeotropes

There are several methods for detecting azeotropes, the classical one being fractional distillation. Others include ebulliometry, vapor-pressure measurement, and examination of vapor-liquid equilibria. After a review of the possible methods, it was decided to use ebulliometry as the primary tool for our investigations. Binary systems of interest could be quickly screened by observing the change in boiling point when the higher-boiling of the two components was added to the lower-boiling. As a check on results obtained by ebulliometry, some of the systems were distilled, and the first fractions collected were checked by gas chromatography to verify the composition of the azeotrope. The use of this approach made it possible to cover the systems selected for investigation quite rapidly and accurately.

Although it was recognized that the composition of an azeotrope is pressure-dependent, our investigations were all carried out at atmospheric pressure, since changes in azeotropic composition are not significant in the relatively small pressure range involved in aerosol packaging. If a greater pressure range were involved, the desired information could be obtained by vapor pressure - composition measurements at various temperatures (i.e., pressure levels).

C. Systems Investigated

At the outset of the study a selected list of compounds was prepared in order of increasing boiling point. This list was in turn prepared from a general list of all compounds in the boiling point range of -45°C. to +50°C. taken from the literature. Most compounds which possessed undesir-

able properties such as high toxicity, reactivity, or cost were eliminated to give the final list shown in Table I. A few compounds which did not meet these standards were retained to provide some indication of general activity toward azeotrope formation amoung the fluorocarbons.

(Table I)

The principal aerosol propellants are fluorocarbons 11, 12, and 114. Candidates for binary systems involving each of these fluorocarbons as a fixed component were selected in accordance with the considerations discussed above.

1. Fluorocarbon 12 Study

All systems in the proper boiling-point range (-43°C. to 0°C.) were investigated, with the exception of 1,3-butadiene. The results of this study are reviewed in Table II. Only two azeotropes were discovered which were not previously known; one with allene and the other with methyl acetylene. Neither of the azeotropes would be suitable as an aerosol propellant, since these hydrocarbons possess high reactivity and are present in large enough proportion to make the azeotropes flammable. A consideration of mixtures of the other components with fluorocarbon 12 further points up the lack of a practical propellant azeotrope. In the case where the azeotropes are nonflammable, the economics are unfavorable, while in other cases where some economic advantage is apparent, they become unacceptable because of toxicity or reactivity. An exception is the dimethyl ether

TABLE I

SELECTED LIST OF CANDIDATES FOR AZEOTROPE STUDY

BOILING POINT °C.	COMPOUND
-42.2	Propane
-40.8	Fluorocarbon 22
-38	Fluorocarbon 115
-34.4	Cyclopropane
-32	Allene
-29.8	Fluorocarbon 12
-24.7	Fluorocarbon 152a
-24.2	Methyl Chloride
-23.7	Dimethyl Ether
-23.3	Propyne
-13.4	Vinyl Chloride
-11.7	Isobutane
-9.2	Fluorocarbon 142b
-6	Isobutylene
-5	1-Butene
-3	1,3-Butadiene
-0.6	n-Butane
+1	cis 2-Butene
+2.5	trans 2-Butene
3.6	Methyl Bromide
3.6	Fluorocarbon 114
6	Vinyl Methyl Ether
6.0	Fluorocarbon 133
8.9	Fluorocarbon 21
9.5	Neopentane
12.2	Ethyl Chloride
21.0	Acetaldehyde
23.8	Fluorocarbon 11
25.0	3-Methyl Butene-1
28	Isopentane
29.9	1-Pentene
31	2-Methyl Butene-1
31.5	Methyl Formate
32	Furan
34.6	Ethyl Ether
35.4	Isopropyl Chloride
36.2	n-Pentane
36.4	2-Pentene
38	Ethyl Bromide
38.4	2-Methyl Butene-2
40.1	Methylene Chloride
47.1	Fluorocarbon 113

azeotrope, which is suitable as a propellant, but does not have the economic advantage of the propellant blend[1].

(Table II)

2. Fluorocarbon 11 Study

Table III lists the large number of fluorocarbon 11 systems studied. Despite the extensive investigation of this fluorocarbon, no new azeotropes were discovered. There are only two known azeotropes of fluorocarbon 11, one with acetaldehyde, and the other with methyl formate, both of which have undesirable properties. It is interesting to note that both of these compounds are highly associated in the liquid phase. Evidently, fluorocarbon 11 has a very low level of intermolecular attraction by itself and has little interference effect on intermolecular attractions when present in mixtures with other compounds. Thus an azeotrope would be expected to form only when the second components have an unusually high level of intermolecular attractions that can be impeded by the presence of the fluorocarbon 11.

(Table III)

3. Fluorocarbon 114 Study

In contrast to fluorocarbon 11, which shows little azeotropic activity, and fluorocarbon 12, which forms a limited number, fluorocarbon 114

TABLE II

A REVIEW OF COMPOUNDS TESTED FOR AZEOTROPES WITH FLUOROCARBON 12

Second Component	Results of Study	Remarks *
Propane	No azeotrope found	25% Fluorocarbon 12 Boiling Point -41.4°C.
Fluorocarbon 22	Azeotrope previously reported (11)	
Fluorocarbon 115	No azeotrope found	
Cyclopropane	No azeotrope found	
Allene	Azeotrope discovered	50-60 mole % Fluorocarbon 12 Boiling Point -34 to -36°C.
Fluorocarbon 152a	Azeotrope previously reported (12)	77.6% Fluorocarbon 12 Boiling Point -30.5°C.
Methyl Chloride	Azeotrope previously reported (13)	At 5380 mm: 78% Fluorocarbon 12 Boiling Point -25°C.
Methyl Ether	Azeotrope previously reported (13)	At 2340 mm: 90% Fluorocarbon 12 Boiling Point -0°C.
Propyne	Azeotrope discovered	13-14% Fluorocarbon 12 Boiling Point -31.5 to -32.5°C.
Vinyl Chloride	No azeotrope found	
Isobutylene	No azeotrope found	
1-Butene	No azeotrope found	
n-Butane	No azeotrope found	

* Compositions are in weight %.

TABLE III

FLUOROCARBON 11

List of Compounds Studied Which Do Not Form Azeotropes

Butadiene	2-Methyl Butene-1
n-Butane	Furan
trans 2-Butene	1-Pentene
Methyl Bromide	Ethyl Ether
Fluorocarbon 114	Isopropyl Chloride
Fluorocarbon 133	Vinyl Ethyl Ether
Fluorocarbon 21	n-Pentane
Neopentane	2-Pentene
Ethyl Chloride	Ethyl Bromide
3-Methyl Butene-1	2-Methyl Butene-2
Isopentane	Methylene Chloride

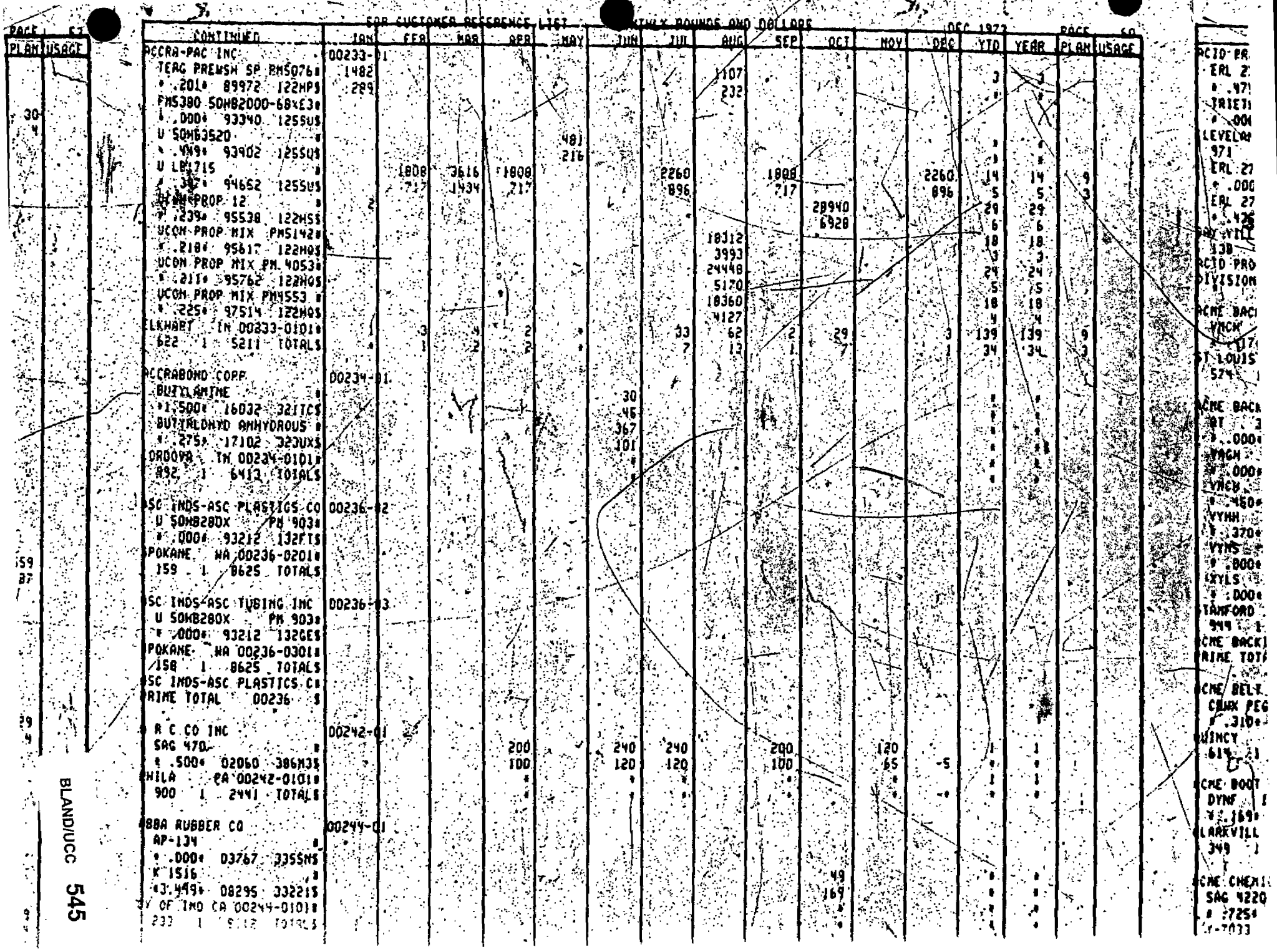
Known Azeotropes of Fluorocarbon 11

Second Component	Boiling Point of Azeotrope	Composition of Azeotrope	
Acetaldehyde	15.6°C.	55% By Weight Fluorocarbon 11	(8)
Methyl Formate	20°C.	82% By Weight Fluorocarbon 11	(8)

forms many azeotropes. The results of the study with this fluorocarbon are given in Table IV. Some of the azeotropes involving fluorocarbons 114 might be of value. These azeotropes and their properties are reviewed in Table V. The azeotropes involving the hydrocarbons are flammable accordind to flammability curves for similar systems[3], thus making them undesirable for aerosol use despite the considerable economic advantage. Conversely, the fluorocarbon 133 system is nonflammable but offered no improved economics. The azeotrope with fluorocarbon 21 could be of some value, since it would be nonflammable and probably economical. Likewise, the ethyl chloride azeotrope, which has been mentioned as a refrigerant[7], may also have possibilities as a propellant.

The reason for the unusual activity of fluorocarbon 114 toward azeotrope formation is probably related to the large number of fluorine atoms present. Evidently the structure of the fluorocarbons 114 molecule makes it very effective in altering the associative forces of other compounds when they are mixed with it.

(Tables IV and V)



CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	PCT
CARSON CHEMICALS INC	13863-01															
HEXYLENE GLYCOL #																
41383 66790$																
ISOPHORONE #																
42842 44572$																
ISOPROPANOL ANHYDROUS#						6541					6580		13	13	30	40
[illegible]						[illegible]					[illegible]		1	1	2	
POTASSIUM [illegible] #											[illegible]		*	*		
70781 66790$											34		*	*		
PROPYLENE GLYCOL IND #							960						1	1		
[illegible]							[illegible]						*	*		
STODDARD FLY [illegible]			[illegible]		[illegible]				[illegible]				2	2		1
82705 44370$			165		165	330			182				1	1		
TERGITOL NON NPX #																
[illegible]																
TERGITOL NPX 10 #																
84931 44572$																
TRIETHANOLAMINE COMM #	9												*	*		
[illegible]	*												*	*		
UCON FLUORO 11 PROP #												87	*	*		
95534 44776$												70	*	*		
UCON FLUORO 12 PROP #												58	*	*		
[illegible]												[illegible]	*	*		
UCON FLUORO 113 [illegible]											[illegible]		-1	-1		
95543 44675$											-485		-*	-*		
UCON PROP VINYL CHLOR#			360			3500	2000	2000	1250			1750	11	11		
[illegible]			[illegible]				[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]		
[illegible]										[illegible]	[illegible]		[illegible]	[illegible]		
99999 66790$										445	330		1	1		
NEW CASTL,IN 13863-0101#	1		1		*	11	3	2	2	2	1	2	31	31	30	42
[illegible]	*		*		*	*	[illegible]	[illegible]	[illegible]	*	[illegible]	*	*	*	[illegible]	
CARSON NEWMAN COLLEGE	13865-01															
DEMURRAGE-CYLINDR CHM#																
[illegible]																
[illegible]																
1810- - -4523-TOT$																
THE CARTER BELT MFG CO	13883-01															
[illegible] #	40								40				*	*		
43205 66790$	18								26				*	*		
SPRINGFLD,NJ 13883-0101#	*								*				*	*		
[illegible]	*								*				*	*		
CARTER INSECTICIDE&CHEM	13888-01															
CRAG SEVIN SPRAY 80 #			22000		22000		11000						55	55		44
[illegible]			[illegible]		[illegible]		[illegible]						30	30		
CRAG SEVIN 80% DUST #																40
21450 44471$																
WALLACE ,NC 13888-0101#			22		22		11						55	55		84
[illegible]			[illegible]		[illegible]		[illegible]						30	30		
L E CARTER CO INC	13892-01															
ACETONE #							350		2100	18952			21	21		
11212 11702$							[illegible]		[illegible]	[illegible]			[illegible]	[illegible]		
BUTANOL BUTYL ALC #							[illegible]						[illegible]	[illegible]		
15355 11702$							59						*	*		
N BUTYL ACETATE #										400			*	*		
15621 11702$										[illegible]			*	*		

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN
CARSON CHEMICALS INC 13863-01															
LOCK PROP VINYL CHLOR#			1750		1750	3500			5250			1750	14	14	25
55774 54776$			389		378	765			1142			377	3	3	5
MISC UNIDENTIFIED #															
59999 54572$															
NEW CASTL,IN 13863-C1C1#	*	1	2	1	3	4	1	*	6	*		4	23	23	46
23AC- - -5224-TOT$	*	*	*	*	1	1	*	*	1	*	-*	1	6	6	7
THE CARTER BELL MFG CO 13883-01															
ISOPROPANOLAMINE MIX #				40							80		*		
43205 33859$				16							33		*		
SPRINGFLD,NJ 13883-C101#				*							*		*	*	
C5SC- - -2311-TOT$				*							*		*	*	
CARTER HOTEL DRUG STORE 13886-01															
ISOPROPANOL ANHYDROUS#								355					*	*	
43062 33855$								39					*	*	
CLEVELAND,OH 13886-C101#								*					*	*	
114C- - -3211-TOT$								*					*	*	
CARTER INSECTICIDE&CHEM 13888-C1															
CRAG SEVIN SPRAY EC #	22000										22000		44	44	60
21448 54471$	12320										11611		24	24	32
WALLACE ,NC 13888-C101#	22										22		44	44	60
23JC- - -4111-TOT$	12										12		24	24	32
L E CARTER CO INC 13892-01															
ACETONE #						15312				350	2100	1050	19	19	
11212 117C2$						995				32	189	95	1	1	
BUTANOL BUTYL ALC #									370				*		
15355 117C2$									60				*	*	
N BUTYL ACETATE #				400					400				1	1	
15621 117C2$				58					62				*	*	
BUTYL CELLOSOLVE #				820					820				2	2	
16507 117C2$				188					189				*	*	
CELLOSOLVE #	420							420					1	1	
19512 117C2$	96							93					*	*	
CELLOSOLVE ACETATE #				880					2200	440			4	4	
19552 117C2$				172					429	86			1	1	
DIISOBUTYL KETONE #				370					370				1	1	
27853 117C2$				59					59				*	*	
ETHYL ACET DEN 85-90$#	400			400					400				1	1	
32339 117C2$	60			60					60				*	*	
ISOPROPANOL ANHYDROUS#										355		355	1	1	
43062 117C2$										33		33	*	*	
ISOPROPYL ACETATE 95%#															
43245 117C2$															
METHYL AMYL ALCOHOL #															
46503 117C5$															
METHYL ETHYL KETONE #	720			720		720		360	720	360	360	360	4	4	
46560 117C2$	108			108		108		54	108	54	54	54	1	1	
METHY ISOBUTYL KETONE#									6650				7	7	
47307 117C2$									870				1	1	
PM3654 TRACTS C12 61 #															70
53854 117C2$															7
PM3953 135 BUAC26 62 #					7120								7	7	10
53953 117C2$					820								1	1	1

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CARROLL PRODUCTS INC 13847-01																
NIAX POLYOL LHT 240 #		460		460		460		460				460	2	2		3
40989 $		142		142		143		143				97	1	1		
NIAX POLYOL LHT 67 #		80									40		*	*		
40989 $		34									13		*	*		
FARMINGDL,NY 13847-0101$		1		*		*		*			*	*	2	2		3
0440- - -2122-TOT$		*		*		*		*			*	*	1	1		
CARLTON LABS INC 13861-01																
CBWX PEG 200 #						510							1	1		1
18219 $						132							*	*		
CBWX PEG 1000 #			10										*	*		
18230 $			8										*	*		
CBWX PEG 1540 #						500							1	1		1
18236 $						165							*	*		
CBWX PEG 4000 #						100							*	*		
18241 $						32							*	*		
METAIRIE ,LA 13861-0101$			*			1							1	1		2
1800- - -7214-TOT$			*			*							*	*		
CARSON CHEMICALS INC 13863-01																
ACETONE #			850										*	*		
43441 $			83										*	*		
CBWX PEG 200 #						510							1	1		1
18214 $						132							*	*		
SENTRY CMC F-75-H #												150				
43024 $												104	*	*		
CALCOMIDE CMC-75-H #												-15	-*	-*		
43024 $												-11	-*	-*		
CRAG SEVIN ARBO GR 97#				1000	1000								2	2		2
21437 $				385	385								1	1		
CRAG SEVIN 50 WFC CON$					-1000								-1	-1		1
21434 $					-385								-*	-*		
ETHYLENE OXYGEN #																
43240 $																
ISOPROPANOL ANHYDROUS#																44
43062 $																
PROPYLENE GLYCOL IND #		480											*	*		1
43612 $		81											*	*		
STARBLEND FLY REPELLE#		446	446	446	446	892		446		446			4	4		5
88705 $		168	165	165	168	330		164		165			1	1		
TERG NON NPX #																
84782 $																
UCON FLUORO 12 PROP #											58		*	*		
95838 $											39		*	*		
UCON FLUORO 114 PROP #																
95842 $																
UCON PROPELLANT 114 #											87		*			
95574 $											72					
UCON PROP VINYL CHLOR#	957	1750	5250	3500	2444	1750		3500	1750	1750	1750	1750	26	26		31
95774 $	189	378	1331	756	921	378		765	378	377	377	378	6	6		
NEW CASTLE,IN 13863-0101$	1	3	6	5	5	5		4	2	2	2	2	32	32		88
2390- - -5824-TOT$	*	1	1	1	1	1		1	*	1	*	*	8	8		

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	AVR	PLAN	PCT
CARSON CHEMICALS INC 13863-01																
CRAG SEVIN 50 MFC CON#		1000									1000		2	2		2
21438 AA171$		384									410		1	1		
ISOPROPANOL ANHYDROUS#																44
43062 AA2G0$																
PROPYLENE GLYCOL IND #																1
71612 AA2G0$																
STABILENE FLY REPELNT#	446		446	446	446	892		446	446	446			4	4	3	3
82705 AA170$	164		165	165	165	330		165	165	165			1	1	1	
UCON FLUORO 12 PROP #																
95536 BB376$																
UCON FLUORO 114 PROP #																
95962 BB376$																
U PROP PM3794 VIN CHL#		5250	5250	1750	1750	5250		3522	1761	3511	1750		30	30	15	31
95774 BB376$		1132	1144	388	379	1133		759	380	757	364		6	6	3	
NEW CASTL,IN 13863-0101#	*	6	6	3	2	6		4	2	4	3		36	36	18	87
0360- - -5324-IQT$	*	2	1	1	1	1		1	1	1	1		9	9	4	
THE CARTER BELL MFG CO 13883-01																
ISOPROPANOLAMINE MIX #				40							80		*	*		
43205 JJ359$				16							33		*	*		
SPRINGFLD,NJ 13883-0101#				*							*					
0580- - -2311-IQT$				*							*		*	*		
EDWARD CARTER JR 13884-01																
FXL PZR DOP #							8						*	*		
39473 ZZ6M4$							5						*	*		
BORDENTWN,NJ 13884-0101#							*						*			
0610- - -2413-IQT$							*						*	*		
CARTER INSECTICIDE&CHEM 13888-01																
CG SVN SPRAY 80 4X10 #									7600				8	8	43	43
21448 AA171$									4320				4	4	24	
WALLACE ,NC 13888-0101#									8				8	8	43	43
2300- - -4111-IQT$									4				4	4	24	
L E CARTER CO INC 13892-01																
ACETONE #	9562		1400	1750	29004					28559			70	70	49	71
11212 MM3IS$	622		126	157	1884					1857			5	5	3	
PM4081 SD3A90 19 &1 #			365	365		366		365	366			365	2	2		
14081 D06M1$			39	39		40		39	40			39	*	*		
BUTANOL BUTYL ALC #									370					*		
15355 MM3IS$									60				*	*		
N BUTYL ACETATE #	400				400	400		400		3655			5	5		
15821 MM3IS$	64				64	64		64		494			1	1		
BUTYL CELLOSOLVE #		410						410		410			1	1		
16507 MM3IS$		95						95		95			*	*		
CELLOSOLVE #		420						420		840			2	2		
19512 MM3IS$		92						92		184			*	*		
CELLOSOLVE ACETATE #	1726			440	8174								10	10	13	1
19552 MM3IS$	293			86	1390								2	2	2	
DIISOBUTYL KETONE #																
27852 MM3IS$																
ETHYL ACET DEN 85-90%#	400												*	*		
32339 MM3IS$	60												*	*		
PM3640-PM3134 98% &1 #						400				4500			5	5		
32393 JJ359$						60				581			1	1		
ISOPROPANOL ANHYDROUS#	1328				7238					7300			16	16	16	1
43062 MM3	97				528					550			1	1	1	

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CARRTONE LABS INC 13861-01																
METAIRIE LA 13861-0101#																2
196 7214 TOTAL$																
CARSON CHEMICALS INC 13863-01																
ACETONE #																1
* .000* 11212 112GD$																
CBWX PEG 200 #																1
.000* 18214 112GE$																
SENTRY CMC F-75-M #																
* .000* 19034 123DR$																
CELLOSIZE CMC P 75 M #																
* .000* 19043 45164$																
SEVIN 97.5 OMS #										1000			1	1		2
* .809* 21437 11171$										809			*	*		
SEVIN 50 CTN #									1000				1	1		2
* .410* 21438 11171$									410				*	*		
ISOPROPANOL ANHYDROUS#																44
* .000* 43062 112GD$																
PROPYLENE GLYCOL IND #																1
* .000* 71612 112GD$																
STABILENE FLY REPELNT#		446	892				892			446			3	3	4	4
.370* 82705 11170$		165	330				330			165			*	*	1	
UCON FLUORO 12 PROP #	58												*	*		
* .414* 95538 123CT$	24												*	*		
UCON FLUORO 114 PROP #	87												*	*		
* .816* 95562 123CT$	71												*	*		
U PROP PM3794 VIN CML#	1750	1750	3500		3500	1750	3750	3500	3500	1750	3500	5250	34	34	26	26
* .208* 95774 123CU$	377	364	742		728	364	779	728	674	364	728	1113	6	6	5	
NEW CASTL IN 13863-0101#	2	2	4		4	2	5	4	5	3	4	5	38	38	30	81
590 5224 TOTAL$	*	1	1		1	*	1	1	1	1	1	1	9	9	6	
CARTANS BABY NEWS STORES 13875-01																
HARDN CONTAIN NO EPOX#																
* .000* P6422 342HK$																
SN LEANDR CA 13875-0101#																
233 TOTAL$																
CARSON REED CORP 13880-01																
U SOLVENT MCP PM4814#	53												*	*		
* .415* 95789 186M1$	22												*	*		
SOUTHFLD MI 13880-0101#	*												*	*		
900 5112 TOTAL$	*												*	*		
CART SHOP 13881-01																
METHANOL SYNTHETIC #			358										*	*		
* .092* 45205 386M3$			33										*	*		
NYACK NY 13881-0101#			*										*	*		
900 2132 TOTAL$			*										*	*		
AB CARTER MILL DEVICES D 13882-02																
U LB1145 #												452	*	*		
* .363* 94602 186M1$												164	*	*		
GASTONIA NC 13882-0201#												*	*	*		
900 4123 TOTAL$												*	*	*		

		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	PCT
CARSON PRODUCTS CO	13851-01																
PARA PHENY PHENOL RES																	
. .000. P6122 321EF																	
BAL CYNWD PA 13851-0101																	
296 TOTAL																	
CARRUZOBBI BENEDITTO	13860-01																
ETHYLENE DICHLORIDE																	
. .000. 35102 11293																	
TOUGHKENM PA 13860-0101																	
363 2942 TOTAL																	
CARS INC	13862-01																
L 45 350 CSTKS					8					8			8	.	.		
.2,417. 01070 393AB					19					20			19	.	.		
LAKELAND FL 13862-0101					.					.			.	.	.		
186 4321 TOTAL					.					.			.	.	.		
CARSON CHEMICALS INC	13863-01																
OMAK PEG 200																	
. .000. 18214 11272																	
CELLOSIZE CMC P 75 M																	
. .000. 19043 186M																	
SEVIN 97.5 OMS		-1000												1	1		
. .809. 21437 11171		-809												.	.		
SEVIN 50 CTN													1000	1	1		
. .430. 21438 11171													430	.	.		
SEVIN TECH		1000				1000					1000			3	3		
. .822. 21952 11171		809				829					829			2	2		
ISOPROPANOL ANHYDROUS		2130	6666		6554				6468					22	22		
. .083. 43062 11272		276	522		513				506					1	1		
UCON PROP MIX PM3275							4000							4	4		
. .219. 93275 123CU							992			-135				.	.		
PROPYLENE GLY SENTRY					482									.	.		
. .205. 71619 186M1					99									.	.		
STABILENE FLY REPELNT		892				892			892		892			4	4	4	4
. .370. 82705 11170		330				330			330		330			1	1	1	
TERG NON NPX						480								.	.		
. .225. 09742 186M1						108								.	.		
TRIETHANOLAMINE COMM												47		.	.		
. .390. 88205 186M1												16		.	.		
UCON PROP 12														.	.		
. .000. 99538 123CT														.	.		
UCON FLUORO 114 PROP														.	.		
. .000. 99562 123CT														.	.		
U/PROP PM3794 VIN CHL								1750	7000	1750				11	11	29	29
. .205. 99774 123CU								378	1905	369				2	2	4	
NEW CASTL IN 13863-0101		3	7		7	2	4	2	14	2	2	.	1	44	44	28	28
200 5229 TOTAL		1	1		1	1	1	.	2	.	1	.	.	8	8	6	
CARSONS INC	13869-01																
UTILITY RECEPTACLES				144			45							.	.		
. .868. P1953 213M				91			47							.	.		
DENVER CO 13869-0101				.			.							.	.		
584 TOTAL				.			.							.	.		

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	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
CARSON CHEMICALS INC 13863-01																
ACETONE					1428								1	1		
.104% 11212 123CUS					148								1	1		
SEVIN.8Z.5 50 LB CTN					200					1000			1	1		
.860% 21437 111715					172					860			1	1		
SEVIN 50 CTN									1000				1	1		
.450% 21438 111715									450				1	1		
SEVIN TECH																
.000% 21452 111715																
SEVIN 50% DB						1000							1	1		
.858% 21460 111715						858							1	1		
HEXYLENE GLYCOL				427												
.220% 41583 486M45				84												
ISOPROPANOL ANHYDROUS																
.000% 43062 112725																
PM3852 100.9 61						6560	8686	8752	8627				36	36	39	40
.080% 43098 123CUS						488	808	778	768				2	2	2	
UCON PROP FLUO PM3275																
.000% 53275 123CUS																
UCON PROP FLUO PM3301									280							
.586% 53301 123CTS									170							
PR GLYCOL USP	964				1446								2	2		
.188% 71615 112725	188				282								2	2		
PROPYLENE GLY SENTRY																
.000% 71618 112725																
SEVIN 50W 30% BAG				1020									1	1		
.427% 80443 111715				436									1	1		
6TABILENE FLY REPELNT	908			1362	1362			908		908			5	5		
.370% 82705 111705	336			503	504			336		336			2	2		
TERGITOL NPX								480					2	2		
.240% 84782 112725								115					1	1		
TRIETHANOLAMINE COMM																
.000% 88205 112725																
TRIETHANOLAMINE 99%				47												
.362% 88206 112725				17												
UCON PROP MIX PM 3784	1750		1750	3500	5250		4000	2000	5500	3500	3500	1750	33	33	22	24
.264% 95774 123CUS	450		427	1287	1323		998	500	1375	874	862	449	8	8	15	
NEW CASTL IN 13863-0101	4		2	6	10	8	14	13	16	5	4	2	83	83	61	64
556 1 5224 TOTALS	1		1	2	1	2	2	3	2	1	1	1	17	17	8	
CARSON NATIONAL FOREST 13864-01																
DGA-70																
.000% 22472 386M39																
TAOS NM 13864-0101																
900 1 7525 TOTALS																
CARSONS MFG CO 13865-01																
DMDA8617NT 7																
.000% P4827 211GAS																
LOS ANGEL CA 13865-0101																
678 1 TOTALS									1							
CARSON CHEMICAL 13866-01																
TERGITOL XD																
.283% 84931 186M15					450											
LONG BCH CA 13866-0101					132											
650 1 812 TOTALS																

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CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
CARSON CHEMICALS INC	13863-01															
HEXYLENE GLYCOL #																
* .000* 41583 486M4$																
PM3852 I99.9 81 #			13300										13	13	45	
* .079* 43098 123CU$			1056										1	1	3	
UCON PROP FLUO PM3301#																
* .000* 53301 123CT$																
PR GLYCOL USP #																
* .000* 71615 11241$																
SEVIN 50W 30# BAG #																
* .000* 80443 11171$																
SEVIN 50MC 30#BAG #												1020	1	1		
* .480* 80448 11171$												490	*	*		
STABILENE FLY REPELNT#	908		1362	454									3	3	4	
* .375* 82705 11170$	341		511	170									1	1	1	
TERGITOL NPX #																
* .000* 84782 11241$																
TRIETHANOLAMINE 99% #																
* .000* 88206 11272$																
UCON PROP MIX PM 3794#	1750		5250	2500									10	10	30	
* .247* 95774 123CU$	432		1312	600									2	2	7	
NEW CASTL IN 13863-0101#	3		21	3	1	1		1				2	32	32	79	
556 1 5224 TOTAL$	1		3	1	*	1		1				1	9	*	12	
CARSON CHEMICAL	13866-01															
TERGITOL XD #																
* .000* 84931 186M1$																
LONG BCH CA 13866-0101#																
653 1 8112 TOTAL$																
CARSON INDUSTRIES	13867-01															
DMDJ7016NT #	10000			10000				49740	-270				69	69		
* .109* P4767 211GF$	1600			1350	-350	-350	350	4974	-27				7	7		
DMDJ7018NT #																
.000* P4769 211GU$																
LA VERNE CA 13867-0101#	10			10				50	-*				69	69		
376 1 8112 TOTAL$	2			1	-*	-*	*	5	-*				7	7		
CARSON CHEMICAL CO	13870-01															
TERGITOL NPX #					480			480					1	1		
* .267* 84782 186M1$					125			131					*	*		
TRIETHANOLAMINE COMM #			510										1	1		
* .239* 88205 132GE$			122										*	*		
SAVANNAH GA 13870-0101#			1		*			*					1	1		
611 1 4231 TOTAL$			*		*			*					*	*		
GLEN A CARTE	13878-01															
CELOSZ HEC-QP-10000-H#							50						*	*		
1.160 19056 322RO$							58						*	*		
GLYOXAL 40% #							11						*	*		
1.1[illegible] [illegible] [illegible]							[illegible]						*	*		

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CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CHASE PRODUCTS CO	15055-01															
PROPYLENE GLYCOL IND #					1440								1	1		1
71612 44877$					241								*	*		
PROPYLENE GLY SENTRY #							480	480					1	1		
71619 33741$							90	90					*	*		
PROPYLENE OXIDE #				370									*	*		
71805 44877$				69									*	*		
TRIETHANOLAMINE COMM #				1020			510						2	2		1
88205 44877$				265			133						*	*		
TRIETHYLENE GLYCOL #		1560	520			1040	1560	1040		2600			8	8		2
88505 44877$		351	117			234	351	234		585			2	2		
UCON FLUORO 11 PROP #	69945	-37358	29370	46195	29460	-1000	51435	15100	46080	145280	30180	-1980	423	423		138
95534 44776$	14198	-7583	5842	9310	5802	-218	10130	2953	9280	35359	5945	-520	90	90		
UCON FLUORO 12 REFRIG#	2000					2000				2000			6	6		2
95537 44675$	545					580				562			2	2		
UCON FLUORO 12 PROP #	162475	75511	109960	127485	-286	-1000	154175	226580	48000	46020	2000	112660	1064	1064	2200	2200
95538 44776$	41967	19281	28369	32983	-60	-1103	39324	57863	12329	11099	562	28740	271	271	570	
UCON FLUORO 22 REFRIG#											180		*	*		
95540 44675$											70		*	*		
UCON FLUORO 114 PROP #	60			420	116						120		1	1		1
95547 44776$	53			314	103						98		1	1		
UCON PROP MIX PM 4053#								122940	121260	207600	96080	96580	644	644		
95762 44776$								23719	23704	40196	18465	18634	125	125		
UCON PROP VINYL CHLOR#															300	300
95774 44776$															41	
UCON PROP P XDMET Eo #											100	5880	6	6		
95775 44776$											26	276	*	*		
UCON PROP PROPANE #					200			420					1	1		
95776 44776$					51	-1		62					*	*		
UCON PROP ISOBUTANE #	35621	20766	109187	104831	29183	95865	74432	44794	68505	75709	33374	70864	763	763		300
95777 44776$	1654	997	5020	4888	1968	4399	3429	-20386	3187	4174	1537	3502	14	14		
UCON HYC BLD PM 3951 #	80					960							1	1	750	750
95778 44776$	21					141							*	*	87	
UCON PROP 11 FOR URET#						29240							29	29		
97050 22722$						5936							6	6		
BROADVIEW,IL 15055-0101#	270	60	249	280	60	127	283	411	284	479	162	284	2951	2951	3650	4095
2430- - -5411-TOT$	58	13	39	48	8	10	53	65	49	92	27	51	513	513	735	
CHASE MANHATTAN BANK	15056-01															
PM1611 EG97 62 #										516			1	1		
36151 22934$										78			*	*		
NEW YORK ,NY 15056-0101#										1			1	1		
0430- - -2121-TOT$										*			*	*		
CHATHAM AVIATION CO	15078-01															
PM1717 EG95 65 #							516						1	1		
36155 22934$							79						*	*		
MORRISTWN,NJ 15078-0101#							1						1	1		
0500- - -2313-TOT$							*						*	*		
CHATHAM LABS INC	15079-01															
ALUMINUM ACETATE NIA #									1000		200	3200	4	4		
13139 66790$									540		108	1728	2	2		
RIVERDALE,NJ 15079-0101#									1		*	3	4	4		
0500- - -2313-TOT$									1		*	2	2	2		
CHATHAM MANUFACTURING CO	15082-01															
ISOBUTANOL #	1800	3600	1800	1800	3600	1800	3600	10800		7200	7200	3600	47	47	11	20
42575 33639$	207	559	351	279	558	279	558	1674		1116	1116	558	7	7	2	

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CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CHASE PRODUCTS CO 15C55-01																
UCON FLUORC 12 PROP #	12C27C	149890	118990	22750	113560	126800	107800	26900	18310	118625	6000	5800	936	936	1400	1500
95538 54776$	31685	38303	38234	5650	29144	32347	27239	6958	4363	29465	1681	1206	246	246	357	
UCON FLUORC 22 REFRIG#																
95540 54675$																
UCON FLUORO 114 REFRG#				300									*	*		
95546 54675$				243									*	*		
UCON FLUORC 114 PROP #		120		1200									1	1		1
95562 54776$		100		806			-360						1	1		
UCON PROPELLANT 114 #					3600			4800		2400		6000	17	17		17
95574 54776$					2792			3118		1580		3947	11	11		
PM4575 UPROP11 45% 62#											57140	27820	85	85		85
95593 54776$											11901	5972	18	18		
UCON PROP MIX PM 4053#	-52C	189340	91760	96680	281860	178460	262260	91800	273640	-1820	282080	187280	1933	1933	500	1933
95762 54776$	-244	37660	17775	18408	54379	34424	50590	17693	53079	-4056	53926	36449	370	370	97	
UCON PROP P %DMET ED #																
95775 54776$																
UCON PROP PROPANE #																
95776 54776$																
UCON PROP ISOBUTANE #	35986	57320	110768	68474	163456	107997	98252				213664	90395	946	946	1000	1000
95777 54776$	4746	3381	5196	3212	7668	5005	4514				9822	4148	48	48	49	
UCON HYC BLD PM 3951 #				1960	9200	27582	9200				55315	69263	167	167		167
95778 54776$				294	431	1300	432				2593	2586	8	8		
UCON PROP 11 FOR UREI#																
97C50 54776$																
MISC UNIDENTIFIED #	9578C-191560		340										-95	-95		-570
95999 54677$	19051 -38102		68										-19	-19		
BROADVIEW,IL 15055-C101#	318	267	367	205	600	489	509	177	344	150	620	411	4496	4496	3316	4703
2430- - -5411-TOT$	69	54	70	32	100	83	89	39	68	33	81	57	775	775	583	
UCON FLUORO 12 PROP #			300										*	*		
95538 54776$			120										*	*		
UCON FLUORO 114 PROP #			300										*	*		
95562 54776$			250										*	*		
MAYWOOD ,IL 15055-C102#			1										1	1		
1300- - -5411-TOT$			*										*	*		
CHASE PRODUCTS CO #	318	267	367	205	600	489	509	177	344	150	620	411	4497	4497	3316	4703
DIVISION TOT 15C55-C1$	69	54	70	32	100	83	89	39	68	33	81	57	775	775	583	
CHASE MANHATTAN BANK 15C56-C1																
PM1611 EG57 62 #																
36151 229F1$																
NEW YORK ,NY 15056-C101#																
0430- - -2121-TOT$																
CHATHAM AVIATION CO 15C78-01																
PM1711 EG95 65 #																
36155 229F1$																
MORRISTWN,NJ 15078-C101#																
C500- - -2313-TOT$																
CHATHAM LABS INC 15C79-01																
ALUMINUM ACETATE N1A #	1800	8000	7800	6800		4600	3000	3000	4000	4800		6000	50	50		50
13139 43638$	972	4320	4212	3672		2484	1620	1620	2160	2592		3240	27	27		
RIVERDALE,NJ 15079-C101#	2	8	8	7		5	3	3	4	5		6	50	50		50
0542-C827- -2313-TOT$	1	4	4	4		2	2	2	2	3		3	27	27		

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CHASE PRODUCTS CO	15055-01															
PM4535 UPROP11 45% &2#		25540											26	26		57
95593 54776$		5302											5	5		
UCON PROP MIX PM 4053#	-380	281310	373460	92040	283880	-2560	269465	171800	-100	182640	-640	88820	1740	1740	2500	2554
95782 54776$	-76	53387	72087	16822	53846	-1896	52417	31845	-833	35244	-878	17137	329	329	498	
PM4511 UCON PROP MIX #																
95773 54776$		-47											-*	-*		
UCON PROP PROPANE #	2520												3	3		3
95776 54776$	-371												*	*		
UCON PROP ISOBUTANE #	74900	193479	49975	47038	49975	48918	48885			48885			562	562	2000	2000
95777 54776$	3880	6051	1565	1471	1529	1530	1529			1529			19	19	80	
UCON HYC 8LO PM 3951 #	18400	99057		49510					44894			-49510	162	162	500	537
95778 54776$	862	3098		2272					2059			-2317	6	6	20	
MISC UNIDENTIFIED #																
99999 54877$																
BROADVIEW,IL 15085-0101#	223	741	430	300	515	53	355	358	-25	238	5	48	3242	3242	7530	7823
2430- - -5411-TOT$	40	102	76	42	100	2	62	71	-4	39	1	17	547	547	1214	
UCON FLUORO 12 PROP #																
95538 54776$																
UCON FLUORO 114 PROP #																
95562 54776$																
MAYWOOD ,IL 15095-0102#																
9300- - -5411-TOT$																
CHASE PRODUCTS CO #	223	741	430	300	515	53	355	358	-25	238	5	48	3242	3242	7530	7823
DIVISION TOT 15055-01$	40	102	76	42	100	2	62	71	-4	39	1	17	547	547	1214	
CHASE & SONS	15060-01															
SYNASOL PM 3224 #									366				*	*		
84040 33859$									44				*	*		
RANDOLPH ,MA 15060-0101#									*				*	*		
0110- - -1214-TOT$									*				*	*		
CHATEAU GAY LTD	15070-01															
SORBIC #											50	50	*	*		
82522 66710$											95	95	*	*		
LEWISTON ,NY 15070-0101#											*	*	*	*		
0200- - -3111-TOT$											*	*	*	*		
BERTRAND CHATEL	15076-01															
U LB170XY26 PM2305#			41										*	*		
94364 229FU$			19										*	*		
LEXINGTON,MA 15076-0101#			*										*	*		
0110- - -1213-TOT$			*										*	*		
CHATHAM LABS INC	15079-01															
ALUMINUM ACETATE NIA #	6000	6000	6000	6000	6000	6000	6000	6000	6000		6000		60	60		60
13139 43698$	3240	3240	3239	3240	3240	3240	3240	3239	3239		3240		32	32		
CARBITOL ACETATE #			40										*	*		
18088 33859$			21										*	*		
RIVERDALE,NJ 15079-0101#	6	6	6	6	6	6	6	6	6		6		60	60		60
05C2-0827- -2813-TOT$	3	3	3	3	3	3	3	3	3		3		32	32		

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CHASE PRODUCTS CO		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
		15055-01															
L 45 350 CSTKS	#	40	320	480		160			120			280	40	1	1	*	1
01070	BB3RC$	78	624	936		312			234			546	72	3	3	1	
L 45 60000 CSTKS	#	80		200			680	120	640			40	200	2	2	2	2
01370	BB3RC$	156		390			1326	234	1248			78	360	4	4	3	
LE 461	#		440				880		880	880	440			4	4	5	4
01861	BB3RC$		299				598		598	598	299			2	2	4	
LE 462	#															1	1
01862	BB3RC$															1	
LE 463	#	880		440		880	1760	440	1760					6	6	5	8
01863	SS2RK$	598		299		598	1197	300	1196					4	4	4	
Y 4539	#																
01935	BB3RC$																
L 522	#															*	
02522	BB3RC$																
C8WX PEG 6000	#	50						50					100		*		
18241	BB377$	26						26					37	*	*		
ETHYLENE GLYCOL	#																5
35202	BB377$																
ISOPROPANOL ANHYDROUS	#																10
43062	BB377$																
MORPHOLINE	#		80	40		240	40		40			40		*	*		1
60604	BB377$		58	29		173	29		29			29		*	*		
PROPYLENE OXIDE	#																1
71805	BB377$																
STABILENE FLY REPELNT	#											82		*	*		
82705	DD6M1$											43		*	*		
TRIETHANOLAMINE COMM	#	1020				510	4080		2550	1020			1530	11	11		11
88205	BB377$	265				133	1060		663	265			420	3	3		
TRIETHYLENE GLYCOL	#																4
88505	BB377$																
UCON FLUORO 11 REFRIG	#								1000					1	1		1
95533	DD6M1$								260					*	*		
UCON FLUORO 11 PROP	#			36400	52400	104600	83080	27420	54840	28060	-110069			277	277	400	1000
95534	BB376$	-4		7167	9664	19830	15151	4813	10159	5043	-23883			48	48	80	
UCON FLUORO 12 REFRIG	#	4000	6000	6000	4000	2000	114440	4000	1000					141	141	6	142
95537	BB376$	1124	1492	1661	1125	518	27806	1078	259					35	35	2	
UCON FLUORO 12 PROP	#	103040	-100	111234	3313	230360	-1880	103100		1400	-74000			476	476	900	2000
95538	BB376$	26234	-676	28185	638	55829	-1757	24977	-97	614	-16164		12	118	118	231	
UCON FLUORO 114 PROP	#			116						600				1	1		100
95562	BB376$			93	-2					564	-12			1	1		
PM4235 ISOBUTANE 66%&2	#																
95568	BB376$				-47									-*	-*		
PM4315 PM3963 45% &2	#																
95570	BB376$																
PM4535 UPROP11 45% &2	#																500
95593	BB376$																
UCON PROP MIX PM 4053	#	125080	92940	97140	99360	179800	115880	89440	189940	-540	263500			1253	1253	2200	2200
95762	BB376$	23818	17608	18497	18065	33000	20874	16283	34872	-806	49050	-649	-4	231	231	429	
UCON PROPA PM3417 ISO	#		28020		29520	54640		56560	58600	51280			-6160	272	272		279
95772	BB376$		5836		5853	11167		11215	11618	10167			-1259	55	55		
PM4511 UCON PROP MIX	#																
95773	BB376$																
UCON PROP PROPANE	#																3
95776	BB376$																
UCON PROP ISOBUTANE	#			15840										16	16	1000	1500
95777	BB376$			599										1	1	32	
UCON HYC BLO PM 3951	#		39104		49402									89	89		300
95778	BB376$		1940		1545									3	3		

CONTINUED		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	PUT
CHASE PRODUCTS CO	15055-01																
UCON VINYL CHLORIDE	#				437									*	*		
95798 BB376	$				41									*	*		
MISC UNIDENTIFIED	#							2000	-2000								2
99999 ZZ6UN	$							505	-519					-*	-*		
BROADVIEW,IL 15055-0101	#	234	167	268	238	573	319	283	309	83	80	*	-4	2551	2551	4519	8076
2430- - -5411-TOT	$	52	27	58	37	122	66	59	61	16	9	*	-*	507	507	787	
CHASE & SONS	15060-01																
SYNASOL PM 3224	#																
84060 JJ359	$																
RANDOLPH ,MA 15060-0101	#																
0110- - -1214-TOT	$																
CHASE WALTON ELASTOMERS	15065-01																
K-1215	#		50											*	*		
06772 NN2ST	$		146											*	*		
KH 1200	#										50			*	*		
06980 NN2ST	$										188			*	*		
K 1045	#					400					50			*	*	2	1
08101 NN2TB	$					1140					143			1	1	5	
K 1347	#															1	
08256 HH3TG	$																
K 1516	#					151			100					*	*	2	
08295 NN2TB	$					529			350					1	1	2	
HUDSON ,MA 15065-0101	#		*			1			*		*			1	1	3	1
7410- - -1213-TOT	$		*			2			*		*			2	2	8	
CHASKA CHEMICALS CO INC	15067-01																
TERGITOL MIN FOAM	#												460	*	*		
84589 DD6M1	$												142	*	*		
TERG NON 15 S 9	#	460												*	*		
84698 DD6M1	$	98												*	*		
MINNEAPOL,MN 15067-0101	#	*											*	1	1		
1300- - -5611-TOT	$	*											*	*	*		
CHATEAU GAY LTD	15070-01																
SORBIC	#																
82522 ZZ6M4	$																
LEWISTON ,NY 15070-0101	#																
0200- - -3111-TOT	$																
BERTRAND CHATEL	15076-01																
U LB170XY26 PM2305	#																
94364 CC2FU	$																
LEXINGTON,MA 15076-0101	#																
0110- - -1213-TOT	$																
CHATHAM LABS INC	15079-01																
ALUMINUM ACETATE NIA	#	6000		6000		2600	3600							18	18	48	50
13139 SS238	$	3240		3240		1404	1944							10	10	26	
CARBITOL ACETATE	#																
10088 JJ359	$																
RIVERDALE,NJ 15079-0101	#	6		6		3	4							18	18	48	50
0502-0827- - -2313-TOT	$	3		3		1	2							10	10	26	
CHATHAM MANUFACTURING CO	15082-01																
ISOBUTANOL	#															14	42
42575 SS	$															2	

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	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CHASE & CO	15053-01															
SEVIN 50 CTN #	1000								1500				3	3		2
* .410* 21438 111715	410								615				1	1		
2 ETHYL HEXANOL #						380							*	*		1
* .197* 37005 23359$						75							*	*		
SANFORD FL 15053-0101 #	1					*			2				3	3		3
900 4322 TOTAL$	*					*			1				1	1		
CHASE PRODUCTS CO	15055-01															
L 45 350 CSTKS #	40					200				880		440	2	2	1	1
1.554 01070 123HS$	72					360				1329		664	2	2	2	
L 45 60000 CSTKS #			440										*	*	2	2
1.570 01370 123HS$			691										*	*	3	
LE 46 #			440	440	440	440	1320	1320	2640	1320		3520	12	12		
* .582* 01815 123HS$			277	260	259	260	779	778	1540	752		2007	6	6		
LE 461 #	440	440	1760	440		440	2200	1760				880	8	8	4	4
* .600* 01861 123HP$	277	277	1109	259		259	1298	1038				502	5	5	3	
LE 462 #																1
* .000* 01862 123HS$																
LE 463 #															7	7
* .000* 01863 123HS$															4	
L 522 #																
* .000* 02522 123HS$																
CBWX PEG 6000 #																
* .000* 18241 123CT$																
CELLOSZ HEC QP-09-H #										1200	100		1	1		
* .809* 19091 386M3$										971	81		1	1		
ETHYLENE GLYCOL #																5
* .000* 35202 123CT$																
ISOPROPANOL ANHYDROUS #																10
* .000* 43062 123CT$																
MORPHOLINE #							461						*	*		1
* .475* 60604 123CT$							219						*	*		
PROPYLENE OXIDE #																1
* .000* 71805 123CT$																
STABILENE FLY REPELNT #																
* .000* 82705 186M1$																
TERG NON TMN #						84	84						*	*		
* .446* 84834 123HS$						37	38						*	*		
TRIETHANOLAMINE COMM #	1020										1020	510	3	3	6	6
* .243* 88205 123CT$	280	2									224	113	*	*	1	
TRIETHYLENE GLYCOL #																4
* .000* 88505 123CT$																
UCON FLUORO 11 REFRIG #																1
* .000* 95533 186M1$															350	1000
UCON FLUORO 11 PROP #															67	
* .000* 95534 123SU$																
UCON FLUORO 12 REFRIG #																
* .000* 95537 123SU$																
UCON FLUORO 12 PROP #							-1900				33100		31	31	850	3000
* .242* 95538 123SU$	-1	-126					-361				8028		7	7	198	
UCON FLUORO 114 PROP #												25	*	*	25	100
* .960* 95562 123CU$												24	*	*	13	
PM4235 ISOBUTANE 66862 #																
* .000* 95568 123CT$																
UCON PROP MIX PM 4053 #		-440										36940	37	37	2000	3000
* .172* 95762 123CU$		-83	-183					-17	-250			6825	6	6	382	

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	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
CHASE MANUFACTURING CO 15054-01																
U 50482BOX PM 903				472												
.316 93212 186M1				149												
DOUGLAS MI 15054-0101																
900 5152 TOTALS																
CHASE PRODUCTS CO 15055-01																
L 95 350 CSTKS												880	1	1		1
1.308 01070 123MS												1199	1	1		
L 95 60000 CSTKS																2
.000 01370 123MS																
LE 96		1320		440							440		2	2		
.542 01815 123MS		726		242							229		1	1		
LE 961					440		880	2640	440			1760	6	6	5	5
.538 01861 123MP					242		484	1452	242			897	3	3	2	
LE 963																8
.000 01863 123MS																
L 522		440	90							120			1	1		
2.467 02522 123CT		1056	106							318			1	1		
CBWX PEG 6000								10		20						
.900 18291 123CT								9		18						
CELLOSZ HEC GP-09-M	1200	400		700	300		400	800		1950			6	6		
.791 19091 123CM	972	329		567	243		329	616		1502			9	9		
ISOPROPANOL ANHYDROUS								1								
1.000 93062 123CT								1								
UCON PROP MIX PM3875									21180				21	21		
.212 53275 123CT									4489				4	4		
MORPHOLINE																
.000 60609 123CT																
PROPYLENE OXIDE										379						
.206 71805 186M1										77						
STABILENE FLY REPELNT																
.000 82705 186M1																
TERG BOH TMH																
.000 84834 123MS																
TRIETHANOLAMINE COMM																
.000 88205 123CU																6
UCON REF 11 RET 1T																
.000 95533 186M1																
UCON PROP 11																1000
.000 95534 123SU																
UCON REF 12 RET MISC																
.000 95537 123SU																
UCON PROP 12					37290								37	37	200	3000
.201 95538 123SU	-12				8307	-591			-579	361			7	7	46	
UCON FLUORO 114 PROP																100
.000 95562 123CU																
UCON PROP MIX PM1235																
.000 95568 123CT																
UCON PROP MIX PM 9053								74860		32260			107	107	302	3000
.189 95762 123MS					-36798			12799	-1550	5422	-388		-20	-20	51	
UCON PROPA PM3917 ISO																
.000 95772 123CT																
UCON PROP ISOBUTANE																2000
.000 95777 123CU																
UCON PROP HYDR PM3951																
.000 95778 123CU																

BLAND/UCC 560

SAR CUSTOMER REFERENCE LIST — MONTHLY POUNDS AND DOLLARS — DEC 1970 — PAGE 1940

...TOMER NAME	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLANT	USAGE
CHASE PRODUCTS CO	15055-01															
MORPHOLINE #							461						*	*		
.471 60604 123CTS							217						*	*		
PROPYLENE OXIDE #																
.000 71805 186M1$																
STABILENE FLY REPELNT #																
.000 82705 186M1$																
TERCITOL TMN-6 #																
.000 84834 123HS$																
TRIETHANOLAMINE COMM #																
.000 88205 123CU$																6
TRIETHYLAMINE #											6	60	*	*		
.576 88454 186M1$											4	34	*	*		
UCON REF 11 RET IT #																
.000 95533 186M1$																
UCON PROP 11 #												21553	22	22	98	1000
.213 95534 123SU$												4591	4	4	16	
UCON REF 12 MISC CYL #																
.000 95537 123SU$																
UCON PROP 12 #		105800	-200									39780	145	145	799	800
.224 95538 123SU$		24334	-2478	2433				-1677				9945	32	32	165	
UCON PROP MIX PM4235 #																
.000 95568 123CY$																
UCON PROP 114 #																
.000 95574 123CU$																100
UCON PROP MIX PM 4053 #																
.185 95762 123HS$	-85											33300	33	33	303	303
UCON PROP MIX PM 3417 #												6239	6	6	20	
.213 95772 123CT$												23287	23	23		
UCON PROP PROPANE #												4966	4	4		
1.000 95776 186M1$							1						*	*		
UCON PROP ISOBUTANE #							1						*	*		
.1000 95777 123CU$																2000
UCON PROP HYDR PM3951 #																
.000 95778 123CU$																
UCON VINYL CHLORIDE #																
.000 95788 123CT$																
MISC UNIDENTIFIED #																
.000 99999 486M4$																
BROADVIEW IL 15055-0101 #	1	106	*	*		2	4	*	2	1	2	119	238	238	1200	4929
768 1 5411 TOTALS	1	24	-2	3		1	3	-1	*	1	2	26	56	56	202	
CHASE MANHATTAN BANK	15056-01															
PM1611 EG97 82 #										516			1	1		
.176 36151 132FT$										91			*	*		
NEW YORK NY 15056-0101 #										1			1	1		
.900 1 2121 TOTALS										*			*	*		
CHASE MANAGEMENT CORP	15057-01															
SAG 470 #							80						*	*		
.500 02060 386M3$							40						*	*		
NEW YORK NY 15057-0101 #							*						*	*		
9.45 1 2121 TOTALS							*						*	*		
CHASE & SONS	15060-01															
EX COATNG COMMODITIES #																
.000 P2121 223CK$																5

BLAND/UCC 561

N USAGE	CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN USAGE
	CHASE PRODUCTS CO 15055-01															
	PROPYLENE OXIDE															
	.000 71805 186MI					60										
	TRIETHYLAMINE															
	.567 88454 186MI					45	-11									
	UCON PROP 11															500
	.000 95534 123SU	-366														
	UCON PROP 12		40260											40	40	40 1000
	.221 95538 123SU	-785	10713	-977				-47						8	8	9
	UCON PROP 114															100
	.000 95574 123CU															
0 280	UCON PROP MIX PM 4053		27840	25540										53	53	40 1000
1	.170 95762 123HS	-498	5470	4525	-403									9	9	2
	UCON PROP MIX PM 3417											29500		30	30	
	.212 95772 123CT	-395										6639		6	6	
	UCON PROP PROPANE															50
	.000 95776 186MI															
1 120	UCON PROP ISOBUTANE															2000
0	.000 95777 123CU															
	BROADVIEW IL 15055-0101		68	26	1	2			1		2	31		132	132	90 6962
	768 1 5411 TOTAL	-2	17	4		1	-	-	1	1	-	8	2	31	31	20
4 20																
3	CHASE MANHATTAN BANK 15056-01															
	PM1611 EG97 12															
	.000 36161 132FT															
2 16	NEW YORK NY 15056-0101															
1	946 1 2121 TOTAL															
	CHASE MANAGEMENT CORP 15057-01															
	SAG 470															
	.000 02060 386M3															
	NEW YORK NY 15057-0101															
	945 1 2121 TOTAL															
	CHASE & SONS 15060-01															
5 125	DFD 2005NT P2132															99
2	.000 PIPGT 223CK															
	DFD 6005NT P2132												2			99
	.000 PIRGH 223CK															
2 16	DFD 6603NT P2133															99
1	.000 PISTI 223CK															
	DHDA7702BK 55 P2834															99
	.000 PIWRV 211BT															
2 100	HFD84201NT P2831															99
1	.000 P2NBK 223CK															
	LD PEC PRIMARY COMM		1000					1000						2	2	
	.217 P2132 223CK		203					230								
0 400	LD PEC POWER PRIMARY							300								
6	.243 P2133 223CK							73								
2 75	LD PEC BLACK VPE										200					
2	.290 P2134 223CK										58					
	LD PES NATURAL VPE															
	.000 P2831 223CK															
2 500	LD PES SEMI COND															
0	.000 P2934 211BT															
8 150	MISC SPEC MIE															

BLAND/UCC 562

CSS CUSTOMER REFERENCE LIST MONTHLY [illegible] DEC 1984 PAGE [illegible]

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	PCT
COLGATE PALMOLIVE CO 17949-01																
CARBOWAX PEG L 600 #									180				*	*		
[illegible] 22830$									[illegible]				*	*		
CARBOWAX PEG S 6000 #																
18239 66790$																
CARBOWAX PEG S 6000 #																
[illegible] 22830$																
[illegible] #																
19060 22830$																
ETHYLENE GLYCOL #												45	*	*		
[illegible] 66790$												14	*	*		
[illegible] #																
36770 66790$																
HEXYLENE GLYCOL #																
[illegible] 22830$																
PROPYLENE GLYCOL USP #				60									*	*		
71615 22830$				15									*	*		
PROPYLENE OXIDE #																
[illegible] 66790$																
[illegible] #			12										*	*		
89947 22830$			19										*	*		
UCON LUB 50H8400 #																
[illegible]																
[illegible] #			[illegible]										*	*		
93302 22830$			15										*	*		
UCON LUB LB-1145 #				42									*	*		
[illegible] 22830$				[illegible]									*	*		
[illegible] #		[illegible]											*	*		
94652 22830$		19											*	*		
UCON LUB LB 3000 #		42											*	*		
[illegible] 22830$		19											*	*		
[illegible] #																
97748 22830$																
NEW BRUNS,NJ 17949-0105#		*	*	*					*		*	*	1	1		
[illegible] -TOT$		*	*	*					*		*	*	*	*		
UCON PROP VINYL CHLOR#							[illegible]						*	*		
95774 44776$						84							*	*		
PISCATAWAY,NJ 17949-0107#						*							*	*		
0439-0505- -2332-TOT$						*							*	*		
DEMURRAGE-CYLINDR CHM$																
00998 66790$					-6								-*	-*		
NEW YORK ,NY 17949-0108#																
0430- -2333-TOT$					-*								-*	-*		
UCON FLORIENT BLD MIX#		78000		[illegible]			[illegible]		[illegible]	[illegible]			[illegible]	[illegible]		[illegible]
01503 44776$		12202		24585			7968		4005	-2480			46	46		
TRIETHYLENE GLYCOL #																
[illegible] 22830$																
UCON FLUORO 11 PROP #							[illegible]						[illegible]	[illegible]		
95534 44776$							2684						3	3		
UCON FLUORO 12 PROP #							17569						18	18		
[illegible] 44776$							[illegible]						*	*		
PN4162 [illegible]	104330												104	104		104
95563 44776$	16158												16	16		
UCON PROP ISOBUTANE #							21104						21	21		
[illegible] 44776$							[illegible]						[illegible]	1		
UCON HYC [illegible] #																
95778 44776$																
BALTIMORE,MD 17949-0109#	104	79		159			105		26	-16			457	457		342
0439-0721- -2611-TOT$	16	12		24			[illegible]		[illegible]	[illegible]			[illegible]	[illegible]		

BLAND/UCC 563

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
CRACKIT LEAK MFG LEAK CO	25923-05															
ETH 200PF SD40 A #																1645
.000 31556 123HQ$																
ETH 200PF SD40 B #															251	1700
.000 31567 123HS$															34	
ETH 200PF SD40 SP.GR#	26320	90						41780				.68	.68			
.071 31575 123CT$	1993							2894				.4	.4			
UCON PROP HYDR PM4862#								11580				.12	12			
.056 42560 123HQ$								647				*	*			
UCON PROP HYDR PM4174#		8944										9	.9			
.044 42562 123HQ$		392										*	*			
UCON PROP FLUO PM3270#	36680	37320										74	74	146	300	
.199 53270 123HP$	7273	8114					-661					14	14	27		
UCON PROP FLUO PM3275#						169000			-9880			159	159			
.198 53275 123HQ$						36827	-4115		-1129			31	31			
UCON PROP FLUO PM3288#							1					*	*			
1.000 53288 186M1$							1					*	*			
UCON PROP FLUO PM3424#												*	*			
.000 53424 123HP$			234			-1971						-1	-1			
MORPHOLINE #				461								*	*			
.479 60604 123HP$				221								*	*			
TRIETHANOLAMINE COMM #																
.000 88205 123HS$																
TRIETHANOLAMINE 99% #																
.000 88206 123HS$																
U L870X PM1057#																
.463 94258 132FS$								80				*	*			
UCON PROP MIX PM5304#								37				*	*			
1.000 95522 123HP$							1					*	*			
UCON PROP MIX PM5012 #							1					*	*			
.000 95525 123HP$										2		*	*			
UCON PROP 11 #																
.000 95534 123HQ$																2000
UCON PROP 12 #	36580				33260				80302			150	150	1100		
.236 95538 123HQ$	9869	1708		-2881	8148	-887			19472			35	35	220	3000	
UCON PROP MIX PM5305#							1					*	*			
1.000 95544 123HP$							1					*	*			
UCON PROP MIX PM5306#							1					*	*			
1.000 95545 123HP$							1					*	*			
UCON PROP MIX PM5142#																
.000 95617 123HQ$																
UCON PROP MIX PM 5072#																
.000 95769 123HP$															702	702
UCON PROP MIX PM 3917#															62	
.000 95772 123HP$		-961														
UCON PROP ISOBUTANE #												--	--			
.000 95777 123HQ$																500
UCON PROP HYDR PM3951#																
.000 95778 123HQ$																
UCON PROP N BUTANE #																
.000 95779 123HP$																
UCON PROP HYDR PM4001#	98095	60717	-13945									95	95	1004	1004	
.038 95785 123HP$	1604	2140	-147									3	3	38		
MISC UNIDENTIFIED #	40											*	*			
.025 99999 486M4$	1											*	*			
FRANKLIN KY 25923-0501#	158	107	-13	8	8	164	8	58	75	*		-10	563	563	3263	10911
617 1 3541 TOTALS	23	12	*	-1	-5	34	-3	4	18			-1	82	82	396	

DRESSER IND DRESSR
U 50M8660
.000 93302 1
BRADFORD PA 26025-
981 1 3151 1

DRES IND DRESSR MAG
SAC 470
.000 02060 1
PRIMARY AMYL ALCO
.228 13802 1
BUTYL CELLOSOLVE
.231 16507 1
CELLOSIZ HEC QP10
.741 19047 1
CELLOSIZ HEC QP10
.800 19049 1
ETHYLENE GLYCOL TI
.000 35187 1
ETHYLENE GLYCOL
.085 35202 1
2 ETHYLHEXANOL
.113 37005 1
ISOPROPANOL 91% PR
.000 93048 1
ISOPROPANOL ANHYDR
.069 93062 1
POLYOX RES GR WSR
.000 70308 1
POLYOX WSR-N-3000
.000 70323 9
TEMIK PEST 10G-COT
.000 84182 1
TERGITOL 15-S-3S S
.000 84262 1
TERGITOL NP-14
.215 84714 1
TERG NPX 9181 PM
.000 84773 1
TERGITOL NPX
.210 84782 1
TRIETHYLENE GLYCOL
.211 88505 1
TRIETHYL GLYCOL AT
.000 88506 1
HOUSTON TX 26025-0
192 1 7312 T
TERG NPX 9181 PM
.000 84773 1
HAMBURG PA 26025-0
966 1 2952 T
TERG NPX 9181 PM
.000 84773 1
CHICAGO H IL 26025-0
146 1 5411 T
TERGITOL 08
.000 84381 1

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
PRCCTER & GAMBLE COMPANY 68717-01																
PRCPYLENE GLYCOL USP #		42270				42970							85	85		85
71615 BB342$		5284				5371							11	11		
PROPYLENE GLY SENTRY #	43690		39210	41900		42910		43150		43190	42770	42810	340	340	230	340
71619 BB342$	5461		4931	5238		5364		5394		5399	5347	5352	42	42	29	
TERG NON 15 S 9 #		101024	24720		58540			33680	33120	-7800	66640	33640	344	344	500	520
84698 BB2DD$		13199	3095		7756		-831	4126	4057	-955	8163	4121	43	43	67	
TERG NON 45-S-3 #																
64708 JJ359$																
TERGITOL NONI 15-S-12 #			40										*	*		
84722 DD6M1$			15										*	*		
TRIETHANOLAMINE 99% #																700
88206 BB2DD$																
TRIISOPROPANOLAMINE #										8			*	*		
89255 JJ359$										7			*	*		
UCANE ALKY 11 #								780			390		1	1		3
89849 BB2DD$								120			67		*	*		
UCANE ALKY 12 #																
89850 BB2DD$		-1784											-2	-2		
UCANE ALKY 13 #																1
89851 BB2DD$																
U BUTYL PHENOL 4T FL #	2200			4000	4000				5000			4000	19	19	15	19
89952 BB2DD$	561			1020	1020				1275			1020	5	5	4	
U 50HB280X PM 903#			200										*	*		
93212 CC2FT$			88										*			
U 50HB400 #	2820	14100	-6110	28200									39	39	12	47
93252 BB342$	776	4089	-1770	7755									11	11	3	
U 50HB1000 #			470	17280									18	18	6	22
93337 BB342$			178	6307									6	6	2	
U 50HB2000 #																50
93352 BB342$																
U LB1715 COSM GR #																
94651 BB342$																
U DA1905 #	134200	263300	131860	130720	263240	130560	66020	131120	277320	130660	263140	132280	2054	2054	3000	3000
94702 BB2DD$	23954	46999	23721	23266	46989	23305	11746	23405	49502	23101	46970	23612	367	367	537	
UCON FLUORO 11 REFRIG#																
95533 BB376$																
UCON VINYL CHLORIDE #											150		*	*		
95798 DD6M1$											11		*	*		
VALERALDEHYDE #												3	*	*		
97139 ZZ6M4$												4		*		
MISC UNIDENTIFIED #				50	-50							28	*	*		
99999 ZZ6UN$				250	-250							699	1	1		
CINCINNAT,OH 68717-0101#	240	425	194	247	366	256	583	907	1892	1682	496	283	7572	7572	5918	23639
1200- - -3261-TOT$	35	58	31	53	67	46	77	98	261	213	88	32	1058	1058	923	
UCANE ALKY 12 #																18
89850 BB2DD$																
ONTARIO ,CN 68717-0103#																18
1205-2805- -9240-TOT$																
U LB1715 #						1808		1356		904		904	5	5		5
94652 JJ359$		99				657		492		328		328	2	2		
NILES ,IL 68717-0104#						2		1		1		1	5	5		5
1200- - -5411-TOT$		*				1		*		*		*	2	2		
CBWX PEG 4000 #				500									1	1		1
18239 JJ359$				163									*	*		
CELLOSOLVE #																
19512 JJ359$																
TERG NON 15 S 9 #		7360		7360				7360		14720		7360	44	44	12	44
84698 SS3		1343		1342				1343		2686		134	8	8	2	

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
RUST OLEUM CORP	75547-01															
UCON PROP MIX PM 4053#										1530			2	2		2
95762 54776$										336			*	*		
EVANSTON ,IL 75547-0101#	*		1	1	*	1	1			2			7	7	5	12
1390- - -5411-TOT$	*		*	1	*	*	1			*			3	3	3	
RUTH BERRY PUMP CO	75565-01															
U 50H4260X PM 903#																
93212 225FT$																
MEMPHIS ,TN 75565-0101#																
1800- - -6413-TOT$																
RUTHERFORD HOSPITAL INC	75571-01															
TERG ANI 7 #																
84241 33859$																
MURFREESB,TN 75571-0101#																
1810- - -4532-TOT$																
RUTHERFORD DYE & CHEM CO	75573-01															
SODIUM ACETATE ANHY #	2500	1250	3750	3750	2500	5000	2500	3750	3750	2500	2500	2500	36	36	38	38
81004 43647$	413	206	618	619	412	824	414	619	619	412	412	412	6	6	6	
NEW YORK ,NY 75573-0101#	3	1	4	4	3	5	3	4	4	3	3	3	36	36	38	38
0410- - -2121-TOT$	*	*	1	1	*	1	*	1	1	*	*	*	6	6	6	
RUTLAND FIRE CLAY CO	75576-01															
N BUTYL ACETATE #							1600				-800		1	1		2
15821 33859$							272				-135		*	*		
CARBITOL PM 600 #							1880				-940		1	1		2
18017 33859$							450				-225		*	*		
DIBUTYL PHTHALATE #							2880				-1440		1	1		3
24154 33859$							735				-366		*	*		
GLYOXAL 40% #							100						*	*		
40751 33859$							42				-41		*	*		
SODIUM ACETATE ANHY #																
81004 1171S$																
RUTLAND ,VT 75576-0101#							6				-3		3	3		7
0580- - -1153-TOT$							1				-1		1	1		
GLYOXAL 40% #			100	150		150		100	150		100	150	1	1		1
40751 33963$			42	63		63		42	63		40	60	*	*		
SODIUM ACETATE ANHY #					250									*		1
81004 33859$					41								*	*		
GASTONIA ,NC 75576-0102#			*	*	*	*		*	*		*	*	1	1		2
0585-0915- -4123-TOT$			*	*	*	*		*	*		*	*	*	*		
RUTLAND FIRE CLAY CO #			*	*	*	*	6	*	*		-3	*	4	4		9
DIVISION TOT 75576-01$			*	*	*	*	1	*	*		-1	*	1	1		
RUTLAND PLASTICS	75578-01															
DIETHYLENE TRI HIPURT#																
26233 33859$																
DIETHYLENE TRI COM GR#																1
26237 33857$																
EXL PZR NODP MFG #	450	450	1180										2	2		3
39170 11813$	106	106	277										*	*		

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	POT
RUST LICK INC 75546-01																
DIETHYLENE GLYCOL #																
26018 BB3DJ$																
U QUENCHANT A PM4189#																1
54189 CC2FQ$																
MORPHOLINE #	460								460				1	1		1
60604 CC2FS$	261								261				1	1		
POLYAMINE T NEW #																
70060 CC2FS$																
POLYAMINE T #																
70061 CC2FS$																
POLYAMINE T NV #		36380		37110			38280					37780	150	150	190	201
70068 CC2FS$		5093		5195			5359					14356	30	30	27	
PROPYLENE GLY SENTRY #																
71619 JJ359$																
TERG NON 15 S 9 #						460		920		1840	920	920	5	5		5
84698 DD6M1$						90		179		359	179	179	1	1		
TERG NON NPX #		480	960	480		480							2	2		5
84782 BB3DJ$		107	215	108		107							1	1		
TRIETHANOLAMINE COMM #		4660		4800			4845		4720		4620		24	24	12	25
88205 CC2FS$		1049		1080			1066		1062		1039		5	5	3	
TRIETHANOLAMINE 99% #																5
88206 CC2FS$																
U SGHB660 #																
93302 DD6M1$																
GRANITVLL,MA 75546-0102#	1	49	1	50		1	51	1	13	39	13	39	257	257	272	351
0110- - -1213-TOT$	*	8	*	8		*	8	*	3	6	3	15	51	51	41	
RUST OLEUM CORP 75547-01																
BUTYL CELLOSOLVE #																
16507 JJ359$																
CELLOSZ HECQP-15000-H#		50											*	*		
19061 QQ6M3$		52											*	*		
CELL ACET URETHANE GR#	2200				2200					880			5	5		5
19549 JJ359$	462				462					198			1	1		
TETRAETH PENTAMINE #															5	8
85408 MM2PH$															3	
UCON PROP MIX PM 4053#		35800	65140		97220	64780	93920	165580	63940	100580	103400	104980	895	895	1000	1000
95762 BB376$		6908	12556		18520	11971	17355	30596	-4110	18586	19107	19399	151	151	195	
EVANSTON ,IL 75547-0101#	2	36	65		99	65	94	166	64	101	103	105	901	901	1005	1013
2420- - -5411-TOT$	*	7	13		19	12	17	31	-4	19	19	19	152	152	198	
RUST PROOFING & METAL 75549-01																
UCAR 101 #																
03661 PP3SJ$																
CAMBRIDGE,MA 75549-0101#																
7410- - -1213-TOT$																
RUTHERFORD DYE & CHEM CO 75573-01																
SODIUM ACETATE ANHY #	1250	1250	1250	2500	2500	2500	1250	2500	3750	2500	1250	1250	24	24	40	40
81004 SS247$	43	219	218	438	438	438	219	438	656	437	218	219	4	4	7	
NEW YORK ,NY 75573-0101#	1	1	1	3	3	3	1	3	4	3	1	1	24	24	40	40
0410- - -2121-TOT$	*	*	*	*	*	*	*	*	1	*	*	*	4	4	7	
RUTLAND FIRE CLAY CO 75576-01																
SAG 470 #				440									*	*		
02060 NN2RU$				207									*	*		
N BUTYL ACETATE #		800		1200					400			400	3	3		3
15821 JJ359$		140		210					70			76	*	*		

SAR CUSTOMER REFERENCE LIST — MONTHLY POUNDS AND DOLLARS — DEC 1968 — PAGE (6)

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PRIOR	PUC
WEST CLTON CORP 75547-01																
TETRAETH PENTAMINE #															2	
* .CCC* E54CE 322PC$															1	
TRIETHYLAMINE #								90					*	*		
* .CC7* EE454 221IC$								60					*	*		
DCLR DROP MIX PK 40530	103680	141240	174560	103200	207180	97720	130920	98720	102000	139080	144580	108800	1551	1551	1000	1500
* .1E1* 55762 123H3$	15936	26103	31903	18539	35881	17555	23520	17736	18763	24924	25573	15747	280	280	191	
EVANSTON IL 75547-01016	128	141	176	104	232	98	131	99	104	141	145	110	1599	1599	1093	1513
435 5411 TOTAL$	25	26	32	19	41	18	24	18	19	24	26	20	294	294	216	
MIDWEST PACKAGING CO 75560-01																
STYR-CP CRYSTAL #																
* .CCC* P1313 211AM$																
STYR-IMP MT HI MLD RC#					-300								-*	-*		
* .17C* P1743 211AM$					-51								-*	-*		
STYR SUBSTNC IMP MAT #																
* .CCC* P1393 211AM$																
MEMPHIS TN 75560-01016					-*								-*	-*		
457 6413 TOTAL$					-*								-*	-*		
NATIONAL DYE & CHEM CO 75573-01																
SODIUM METABI ANHY #	1250	1250	1250	2750	2750	2500	1500	1500	1250	6270	2500		25	25	32	42
* .17C* 01CC4 442A1$	219	219	218	481	482	438	263	262	218	1057	437		4	4	5	
YONKERS NY 75573-01016	1	1	1	3	3	3	2	2	1	6	3		25	25	32	42
444 5161 TOTAL$	*	*	*	*	*	*	*	*	*	1	*		4	4	5	
PITTS FARM & CITY DISTR 75574-01																
SEA PL*-REC-SESSTR #																
* .CCC* P3251 221CC$				-434									-*	-*		
JEFFERSON IO 75574-01016																
282 TOTAL$				-*									-*	-*		
OUTLAND PIPE CLAY CO 75576-01																
STYR-CP CRYSTAL #									450				*	*		
* .15C* P1713 211AM$									70				*	*		
STYR-MLD RS MED IMP #						450	-450									
* .CCC* P1731 211AM$						173	-173									
SAC 47C #								440					*	*		
* .47C* C2C4C 384M3$								207					*	*		
N BUTYL ACETATE #			400				400	359				798	2	2		3
* .15C* 35621 233S5$			76				76	75				152	*	*		
BUTYL CELLOSOLVE ACET#												39	*	*		
* .25C* 16625 4E6M4$												15	*	*		
CARBITOL PM ECC #			470					470				940	2	2		2
* .25C* 18C17 233S5$			120					120				239	*	*		
DIBUTYL PHTHALATE #			960					480				960	2	2		4
* .27C* 24154 233S5$			264					132				264	*	*		
GLYOXAL 40% #			50				54					54	*	*		
* .40C* 40751 443E3$			20				22					22	*	*		
TERBITOL 15-S-5 #												42	*	*		
* .31C* 54454 1E6M1$												13	*	*		

SAR DISTOMER REFERENCE LIST — MONTHLY POUNDS AND DOLLARS — DEC 1969 — PAGE 6979

ITEM/ED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	PCT
COMP	79547-01															
[illegible]			39													
[illegible] 32315			14													
[illegible]			30	60	90											
[illegible] 32315			20	41	60											
[illegible] PR 90534	110920	197220	139780	137800	68820	146580	161960	160180	119390	168720	130420	32880	1640	1640	1	2900
32315	19925	27265	22862	21653	11994	-27751	27468	27371	19932	29022	22013	22881	279	279	320	
79547-01D1	112	195	135	190	69	189	162	162	121	172	199	139	1696	1696	1683	2985
[illegible] TOTAL	20	29	29	22	12	34	28	28	21	30	27	23	296	296	391	
SUPP CO	79565-01															
CRYSTAL																
[illegible] 211AP																
[illegible]		30000											30	30		
[illegible] 211AP		5250											5	5		
[illegible]											35900		36	36		
[illegible] 211AP											5929		5	5		
[illegible] EMP MAT																
[illegible] 211AP																
[illegible] 79565-01D1		30									36		64	64		
[illegible] TOTAL		5									6		11	11		
INC	79570-01															
[illegible] 85										1	519		1	1		
[illegible] 186415											80					
[illegible] 79570-01D1											1		1	1		
[illegible] TOTAL																
[illegible] & CHEM CO	79573-01															
ACETATE AMMY	2500		2500	5000	5000	2500		5000	5050	9950	-2500	50	30	30	28	99
[illegible] 121974	937		935	875	825	938		875	896	898	-937	9	5	5	9	
[illegible] 79573-01D1	3		3	5	5	3		5	5	5	-3		30	30	28	99
[illegible] TOTAL				1	1			1	1	1			5	5	9	
CLAY CO	79576-01															
CRYSTAL																
[illegible] 211AP																
[illegible]				990												
[illegible] 39366				203												
[illegible]						32			357							
[illegible] 386A3						7			42							
ACETATE				1197			1197						2	2		
[illegible] 23159				233			239									
ACETATE				39	932											
[illegible] 98699				15	108											
[illegible] 600				946				973				973	2	2		
[illegible] 23159				242				121				121				
[illegible] -52000-M	100			50			50									
[illegible] 39366	96			52			91									
[illegible]				1955			1955					965	3	3		
[illegible] 23159				400			400					133				
[illegible]				54				54								
[illegible] 11363				22				20								
[illegible]							92									
[illegible] 186415							13									
[illegible] MET				658			1910						8	8		
[illegible] 32274				1152			293						1	1		

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
RUST OLEUM CORP	75547-01															
PM4996 CS AC 99% #																
* .000* 19550 323UI$								890					1	1		
CELLOSOLVE ACETATE #								205					*	*		
* .230* 19552 323IS$																
CYCLOHEXANONE #																
* .000* 22052 323IS$																
UCAR LATEX 391 #						222							*	*		
* .514* 43913 386M3$						114							*	*		
TERGITOL 15-S-9 #					16								*	*		
* .813* 84698 186M1$					13								*	*		
TETRAETH PENTAMINE #		463	463			463							1	1		
* .657* 85408 3211C$		303	303			306							*	*		
TOLUENE #							1						*	*		
1.000 87207 323IS$							1						*	*		
TRIETHYLAMINE #	90												*	*		
* .667* 88954 3211C$	60												*	*		
UCON PROP MIX PM 4053#	126340	171940	236200	69900	110500	143540	186740	189320	279740	112300		79200	1706	1706	1751	1751
* .168* 95762 322PC$	21528	30816	43611	11988	12941	24175	31192	31833	46388	19155		12610	286	286	301	
EVANSTON IL 75547-0101#	129	193	238	70	113	165	188	211	281	114		101	1802	1802	1791	1801
639 1 5411 TOTALS	23	37	44	12	14	31	32	38	47	20		20	315	315	311	
A P RUTH & CO	75564-01															
U 50HB280X PM 903#							92						*	*		
* .976* 93212 186M1$							20						*	*		
HOUSTON TX 75564-0101#							*						*	*		
197 1 7312 TOTALS							*						*	*		
RUTH BERRY PUMP CO	75565-01															
GP PO STYR MOLDNG CRY#																
* .000* P1713 211AM$																
HI IMP EXT APPLIAN NT#																
* .000* P1741 211AM$																
HI IMP STYR GP NT #																
* .000* P1743 211AM$																
HI IMP EX PACKAGNG NT#																
* .000* P1746 211AM$																
RUB MOD STY SUB MAT #																
* .000* P1793 211AM$																
PVC CMPDS RGD GR STND#																
* .000* P7711 211AP$										1			*	*		
MEMPHIS TN 75565-0101#																
997 1 6913 TOTALS													*	*		
RUTHRAUFF INC	75570-01															
PM1717 EG95 85 #							1557					1038	3	3		
* .169* 36155 186M1$							256					182	*	*		
PITTSBURG PA 75570-0101#							2					1	3	3		
512 1 3151 TOTALS							*					*	*	*		
RUTHERFORD DYE & CHEM CO	75573-01															
SODIUM ACETATE ANHY #																44
* .000* 81009 1214?$																
NEW YORK NY 75573-0101#																44
919 1 2121 TOTALS																

BLAND/UCC 570

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
RUST OLEUM CORP	75547-01															
VMCH TYPE SOLVENT RES#			300		300		250	500			500		2	2		5
# .445# P7222 321EB$			125		125		127	222			225		#	#		
VYHH TYPE SOLVENT RES#		250	250			250		500					1	1		
# .347# P7223 321EB$		84	84			84		182					#	#		
ZKU 0624 #			663	663				563	375	375	375		3	3		
# .842# P8035 321EF$			374	439				551	420	293	293		2	2		
BUTYL CELLOSOLVE #							37			37			#	#		
# .676# 16507 323UX$							25			25			#	#		
CELLOSZ HECQP-15000-H#																
# .000# 19061 386M3$																
CZ HEC QP-4400-H #										50			#	#		
#1.140# 19096 386M3$										57			#	#		
CELLOSOLVE #																100
# .000# 18512 186M1$																
CELL ACET URETHANE GR#		446	1784		892		1338		446	892			6	6		
# .244# 19548 323UI$		109	437		219		328		109	210			1	1		
PM4446 CS AC 88% #																
# .000# 18550 323UI$																
CELLOSOLVE ACETATE #						882							1	1		
# .244# 19552 323IG$						218							#	#		
CYCLOHEXANONE #																
# .000# 22052 323IG$																
UCAR LATEX 341 #				487		44							1	1		
# .245# 43813 386M3$				114		16							#	#		
MORPHOLINE #						40				32			#	#		
#1.184# 60604 132GE$						41				45			#	#		
TERGITOL 15-S-9 #	16												#	#		
# .750# 84688 186M1$	12												#	#		
TETRAETH PENTAMINE #					463				463				1	1		
# .674# 85408 321IC$					312				312				#	#		
TOLUENE #																750
# .000# 87207 323IS$																
TRIETHYLAMINE #																
# .000# 88454 321IC$																
UCON PROP MIX PM 4053#	122100	81820	138900	156840	116360	174160	124060	114360	152840	196220	121640	159740	1659	1658	1701	1900
# .176# 95762 322PC$	20398	16728	26230	26859	20802	31755	22609	20238	27534	35067	19238	24288	281	291	287	
EVANSTON IL 75547-0101#	122	83	162	158	139	176	126	132	155	222	123	160	1756	1756	1738	3142
639 1 5411 TOTAL$	20	17	34	27	28	32	23	27	28	43	20	24	324	324	300	
RUSTOL CORP	75548-01															
CELLOSZ HECQP-52000-H#									50				#	#		
#1.180# 19065 322RD$									59				#	#		
MIDWAY CY CA 75548-0101#									#				#	#		
653 1 8112 TOTAL$									#				#	#		
R P RUTH & CO	75564-01															
U BOX 8280X PM 903#							478						#	#		
# .366# 83212 186M1$							175						#	#		
HOUSTON TX 75564-0101#							#						#	#		
197 1 7312 TOTAL$							#						#	#		
RUTH BERRY PUMP CO	75565-01															
HI IMP STYR EXTRUS NT#																
# .000# P1741 211JT$																
HI IMP STYR GP NT #																
# .000# P1743 211JT$																

CONTINUED
SCH GLIDDEN DURKEE
FXL PZR DOP
.000# 38473
METHYL CELLOSOLVE
.236# 46825
MORPHOLINE
.000# 60604
PROPYLENE OXIDE
.000# 71805
LOS ANGEL CA 75811
170 1 8112
BKR 2620
.489# P2009
BKS 2600
.850# P2021
CKM 1634
.000# P3806
CKM 2400
.397# P3811
CKM 2432
.410# P3813
CKM 5254
.683# P3814
CKR 0405
.000# P3882
CKR 0406
.000# P3883
CKRB0406
.496# P3884
ERL 2774
.476# P5781
BUTYL PHENOL RES
.000# P6135
EPOXY LIQUID RES
.000# P6411
THERMOSETTING ACI
.652# P6811
UCAR BIS PHENOL
.000# P6823
VMCH TYPE SOLVEN
.390# P7222
VYHH TYPE SOLVEN
.338# P7223
VAGH TYPE SOLVEN
.496# P7225
DISP RESIN OYNM
.280# P7316
PVA OTHR THAN GU
.000# P7412
PVB RESINS XYHL
#1.050# P7511
L 45 350 CSTKS
.000# 01070
L 45 1000 CSTKS
#2.438# 01100
SAG 47
.000# 02050

CONTINUED	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YTD	YEAR	PLAN	USAGE
RUST LICK INC	75546-01														1	
TERGITOL NPX #															*	
* .000* 84782 123DR$							42						44	44	25	
ANAHEIM CA 75546-0103#	2						4						4	4	3	
653 1 8112 TOTAL$	*															
RUST LICK INC #	2	40	1	40		42	42		40		41		248	248	140	
DIVISION TOTAL 75546-01$	1	4	*	4		4	4		4		4		25	25	14	
RUST OLEUM CORP	75547-01															
DPM 2103 #		17150	6850	24000				23900			24000		96	96	61	
* .322* P3809 321EF$		6003	2398	7500				7469			7500		30	30	19	
VMS TYPE SOLVENT RES#				500			500		500		950		2	2	1	
* .490* P7221 321EB$				245			245		245		466		1	1	*	
VMCH TYPE SOLVENT RES#		500					500	500			500	500	3	3	1	
* .460* P7222 321EB$		225					225	225			225	225	1	1	*	
VMH TYPE SOLVENT RES#	500						500		500		500		2	2		
* .370* P7223 321EB$	185						185		185		185		*	*		
WAGH TYPE SOLVENT RES#								200					*	*		
* .550* P7225 321EB$								110					*	*		
ZKU 0624 #		563	525		1126				413	375		375	3	3	1	
* .764* P9035 321EF$		439	410		878				314	285		255	2	2	*	
N BUTYL ACETATE #								1596					2	2		
* .216* 15821 323IS$								344					*	*		
BUTYL CELLOSOLVE #								830					1	1		
* .251* 16507 323UD$								208					*	*		
CZ HEC QP-4400-H #										50	50		*	*		
1.160 190% 386M3$										58	58		*	*		
CELL ACET URETHANE GR#	446	446	892	892	892	892	892		867	446	892		8	8		
* .247* 19549 323UT$	112	111	223	223	223	205	223		217	103	223		1	1		
CELLOSOLVE ACETATE #						892							1	1		
* .250* 19552 323IS$						223							*	*		
ETHYL ACET 99.5BLR GR#								37					*	*		
.622 32310 323IS$								23					*	*		
UCAR LATEX 341 #																
* .000* 43913 386M3$																
MORPHOLINE #		32			41	41				41			*	*		
1.026 60604 132GE$		45			38	38				38			*	*		
PROPYLENE OXIDE #								34					*	*		
.735 71805 112SA$								25					*	*		
TERGITOL 15-S-9 #																
* .000* 84698 186M1$																
TETRAETH PENTAMINE #						463	463	463			463	1852	4	4		
* .668* 85408 321TC$						306	315	315			315	1222	2	2		
UCON PROP MIX PM 4053#	23140	95200	37320	221330	-39020								890	890	1800	
* .170* 95762 322PC$	4081*	1524*	6193*	35855	-7492	129		9640					151	151	306	
EVANSTON IL 75547-0101#	240	114	382	247	-37	2	3	28	2	1	27	3	1011	1011	1869	
768 1 5411 TOTAL$	41	22	65	44	-6	1	1	13	1	*	9	2	193	193	326	
RUSTOL CORP	75548-01															
CELLOSZ HEDQP-52000-H#																
* .000* 19065 322RD$																
MIDWAY CY CA 75548-0101#																
653 1 8112 TOTAL$																
RUTGERS CHEM & METALS IN	75553-01															
VMS TYPE SOLVENT RES#						4000		6000					10	10		
* .446* P7221 321EB$						1820		2640					4	4		

CONTINUED	JAN
SCM GLIDDEN DURKEE D	75811-03
CZ HEC QP-4400-H #	
* .740* 190% 322PB$	
CELLOSOLVE #	7857
* .159* 19512 323IS$	12%
CELL ACET URETHANE GR#	892
* .230* 19549 323UT$	223
CELLOSOLVE ACETATE #	8149
* .168* 19552 323IS$	1353
DIACETONE ALCOHOL #	
* .130* 23002 321IS$	
DIBUTYL PHTHALATE #	
* .000* 24054 323IS$	
DICYCLOPENTADIENE #	
* .000* 25214 334S4$	
DIETHYLENE GLYCOL #	18906
* .069* 26018 334S4$	1228
DIETHYLENETRIAMINE HP#	
* .000* 26233 322PC$	
DIISOBUTYL KETONE #	
* .150* 27853 323IS$	
DMAPA 85% #1 #	16815
* .250* 28013 321TC$	4203
DIPET ETOHAMINE ANHY #	
* .654* 29116 322PC$	
DIPROPYLENE GLYCOL #	39597
* .154* 29847 321TC$	5378
ETH ACRYLA 14PPM MMH#	
* .240* 32809 322PA$	
ETHYL BUTYL KETONE #	
* .477* 33042 323IS$	
ETHYLENE GLYCOL #	9452
* .070* 35202 322PB$	662
2 ETHYLHEXANOL #	
* .177* 37005 323IS$	
2 ETHYL HEXOIC ACID #	
* .300* 37141 322PC$	
2ETHYLHX A 15PPM MMH#	
* .000* 37215 322PA$	
FXL PZR 400 #	
* .000* 39235 321IS$	
FXL PZR 1010 #	
.000* 39265 321IS$	
FXL PZR DOP FOOD GR #	
* .000* 39579 321IS$	
HEXYL CELLOSOLVE #	
* .510* 41559 323IS$	
HEXYLENE GLYCOL #	7851
* .169* 41583 322PB$	1295
ISOBUTANOL #	16978
* .065* 42575 321IS$	1104
ISOBUTYL ACETATE #	
* .193* 42608 323IS$	
ISOBUTYL ACRYLATE #	
* .000* 42621 322PA$	
ISOPHORONE #	7879
* .165* 42842 321IS$	1299