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propellent technology developed in the U.S.A. under the regulatory sword, the cost of their partial ban on CFCs has been estimated at about 1% of the U.S.A. total. In Europe, the EEC countries are typified by the U.K. which went from 95 million pounds (43,000 metric tons) of CFCs in 1977 to an estimated 66 million pounds (30,000 metric tons) in 1982. Production volumes in both years were about equal. The loss was compensated by an increase in hydrocarbon usage: from 28 million pounds (12,900 metric tons) to an estimated 38 million pounds (17,000 metric tons). Relatively little pain was caused by this voluntary transition, since the time frame was generous, there was little bad press, and the bulk of the change was handled by the top 20 or so of the 126 contract and marketer fillers. Nearly all of them already had hydrocarbon facilities, at least to some degree. In Norway and Sweden, which now have CFC bans, the process of change was very costly, forcing many smaller firms to go out of business and inviting a huge increase in imports from nearby Denmark and Germany. At this time, no large aerosol-producing country appears in danger of a ban, and there is hope that the CFC/ozone theories may be so strongly modified by new data during the next two or three years that no further political interdictions or bans will take place.

Properties of the CFC and FC Propellents

Because of the current ban on saturated CFC propellents in the U.S.A. only minor coverage will be accorded to P-11, P-12, P-113, P-114 and P-115. The first four are still very important outside the U.S.A., where they were estimated to account for about 480 million pounds (218,000 metric tons) of CFC production in 1980. The forerunner of the line is P-12, followed by P-11 and then (far behind) P-114. Only P-12 and P-114 can be considered as true propellents. P-11 and P-113 are incapable of forming a spray at room temperatures and are commonly thought of as volatile non-flammable solvents.

P-12 is used most commonly at levels between 20 to 50% of the total formula. At 20% the spray is fairly coarse, and light-bodied volatile concentrates are required to get a satisfactory spray down to the end of the can. Such solvents include 1,1,1-trichloroethane, ethanol and isopropanol. If a less volatile concentrate is required, then the minimum level of P-12 will have to be raised to about 25%. Where the concentration of P-12 is relatively small the distillation effect must be

considered. As the dispenser is sprayed, the outage space expands and P-12 vaporizes out of the liquid phase to maintain the equilibrium pressure. The result is a gradual reduction of the per cent P-12 in the liquid phase, becoming more serious near the end of the can since there is less of a reservoir to draw upon. The pressure and delivery rate can be expected to decrease at least slightly as any aerosol is used up, but the effect is more pronounced for products containing low percentages of propellent.

The properties of P-12 are shown in Table VII (Page 324) along with those of other common CFCs. Succinctly stated, it has a vapor pressure that can be tolerated at any concentration (although a "DOT Specification 2P" or "DOT Specification 2Q" can may be needed at levels of over about 70%), it is non-flammable, non-hydrolysable and a rather poor solvent.

On the basis of economics, and perhaps bans or other sanctions, products which used to have 20 to 25% P-12 as the propellent have now been reformulated to contain 3 to 5% CO₂. The spray may be a little coarser, particularly as the package is sprayed down, and perhaps somewhat more sensitive to propellent leakage rates, but otherwise there are very few problems with the transition. Products such as disinfectant/deodorants, wasp and hornet sprays, mothproofers, engine degreasers, carburetor and choke cleaners, bug killers and so forth may be sprayed with either propellent.

The early hair spray formulations typically contained 35% ethanol-based concentrate, plus 65% of a propellent blend consisting of about 20 parts P-12 and 45 parts P-11. The large percentage of CFCs were used to give elegant sprays (with the valves then available) and only a slight degree of flammability, such as an 8 inch (200 mm) flame in the Flame Projection Tester. However, in the U.S.A. at least, ethanol was only about half as costly as the CFCs, and this economic fact forced CFC levels inexorably downward, until by about 1968 hair spray formulas averaged about 50% concentrate, 26% P-12, 14% P-11 and 10% isobutane A31. The flame projection was now in the 16 to 18 inch (400 to 457 mm) range. During these transitions to less costly, more flammable products, the industry closely monitored the market to see if there were any hazardous consequences. Essentially none were reported. In 1975 through 1977, when the CFCs had to be removed from most U.S.A. aerosols, these data encouraged most marketers to go directly to ethanol/hydrocarbon formulations. A few more cautious ones tried to use CO₂,

but even when up to 20% methylene chloride was included the sprays were still considered too coarse. One very promising formula, using 60% concentrate, 15% methylene chloride, 14% isopentane and 6% CO₂ was abandoned after about 500,000 cans had been made, due to manufacturing hazards involving the isopentane, plus the unreliable supply situation for that ingredient.

The U.S.A. is rather unique in having unlimited supplies of specially denatured ethanol (95v% and anhydrous) at prices of about \$0.30/lb. (\$0.66/kg) on a 1981 and 1982 basis. In the past this has acted to depress the per cent of the relatively expensive CFCs in hair sprays, personal deodorants and other ethanol-based products. But now, since it is 50% more expensive than the Aerosol Grade hydrocarbons, there is at least some incentive to increase the amount of propellant. The cost of ethanol in virtually all other countries is much more than either the CFCs or hydrocarbon gases. Thus, hair sprays and other ethanol formulas are designed with a minimum of this alcohol.

In Mexico, hair sprays have been sold with as little as 12% ethanol and the balance mainly CFCs. In various European countries, a heavy tax is applied to ethanol (also sometimes to isopropanol), with extreme conservation as the end result.

The pressure and densities of various P-12/P-11 blends with anhydrous ethanol are given as Figure 4 and Figure 5 respectively.

The pressure data was developed using a refrigeration filling technique (now obsolete for production purposes in nearly all countries), simply as a means of excluding the partial pressure of air that always enters into the total pressure of pressure-filled aerosol products.

When the percentage of P-12 reaches about 40% to 96%, the products give a finely particled spray pattern, progressing to the area of a 3 μ m average particle size at the 90% level. For particularly good break-up and soft, slow delivery rate sprays, valves with vapor-tap orifices are often used. The chilling or cooling effect is also reduced, and this has been important in such products

TABLE VII

Physical Properties of Chlorofluorinated and Fluorinated Hydrocarbon Propellents (Common Types)

	P-11	P-12	P-21	P-22	P-113	P-114	P-115	P-152a	P-142b
Formula	CCl ₃ F	CCl ₂ F ₂	CHCl ₂ F	CHClF ₂	CCl ₂ FCClF ₂	CClF ₂ CClF ₂	CClF ₂ CF ₃	CH ₃ CHF ₂	CH ₃ CClF ₂
Molecular Weight	137.4	120.9	102.9	86.5	187.4	170.9	154.4	66.1	100.5
Boiling Point (°F)	74.8	21.6	48.1	-41.4	117.6	38.4	-37.7	11.2	15.1
Freezing Point (°F)	-168.	-252.	-211.	-256.	-31.	-137.	-159.	-179.	-204.
Pressure (psi-g. at 70°F)	-1.3	70.2	8.4	122.5	-9.2	12.9	104.9	61.7	29.1
Pressure (psi-g. at 130°F)	24.3	181.0	50.5	300.	3.4	58.8	252.1	176.	92.0
Density (gm./ml. at 70°F)	1.485	1.325	1.323	1.209	1.574	1.468	1.309	0.911	1.119
Density (gm./ml. at 130°F)	1.403	1.191	1.193	1.064	1.493	1.360	1.149	0.813	1.028
Vapor Density at B.P. (gm./1.	5.861	6.258	4.570	4.827	7.330	7.83	8.781	3.38	4.84
Water Solubility (ml./100 gr.)*	20.	5.7	226.	85.			7.4	116.	33.
Kauri-Butanol Number	60.	18.	102.	25.	31.	12.	7.	11.	20.
Solubility Parameter	7.5	6.5	8.0	6.5	7.2	6.2	5.7	7.0	6.8
Hydrolysis in Water (gm./yr.)**	0.005	0.005	0.010	0.010	0.005	0.005	0.005	0.005	0.010
Hydrolysis in 1% Na ₂ CO ₃ (gm./yr.)**	01.20	0.040	330	220		0.010	0.005	0.005	
Hydrolysis in Water with Steel Strips Present (gm./yr.)**	19.	0.82	5.2	0.14		1.4	0.08	0.010	0.20
Flammability Limits in Air v%	none	none	none	none	none	none	none	5.1/19.1	9.0/14.8

*At one atmosphere and 77°F.

**Values expressed as grams HCl/liter of propellant/year, at 68°F when solutions of approximately 25% Propellant, 25% Water and 50% Isopropanol are stored in ampules.

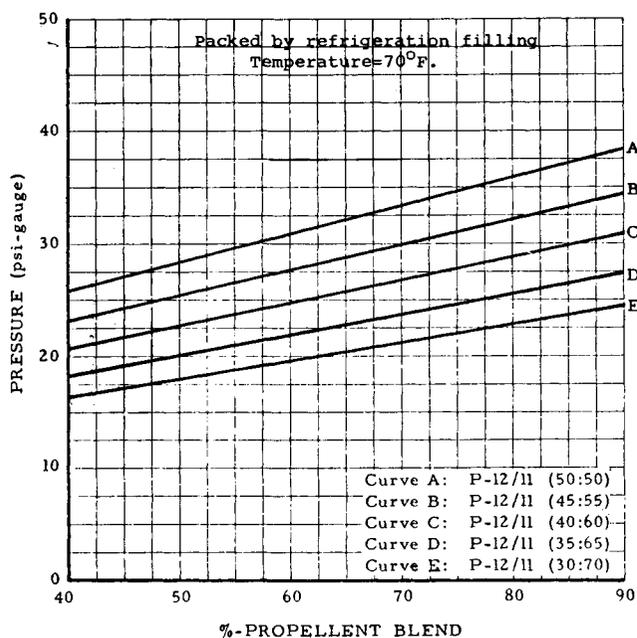


Figure 4. Pressure of CFC-11/12 Mixtures with Ethanol (Air Free)

as feminine hygiene sprays where P-12 is usually over 90%. For these products, a second advantage of the vapor-tap is that the dispensers can be sprayed satisfactorily either upright or inverted.

P-12 comes close to being an ideal propellant, but a significant drawback has been the fact that it is a poor solvent. This is due to the CF_2 moiety in an essentially apolar molecule. Numerous polar materials, such as stearic acid and the other carboxylic acids, triethylene glycol and certain other glycols, certain deodorant chemicals and so forth are essentially insoluble. Some substances are soluble, but have no affinity for the propellant and therefore exert relatively little vapor pressure depressent effect. In formulation of aerosols that contain P-12 as the propellant, it is common to add cosolvents. Methylene chloride, 1,1,1-trichloroethane, P-11, ethanol, isopropanol, acetone and the intermediate ketones have all been used for this purpose.

P-11 has been used in aerosols almost as long as P-12. It may have been used first in 1946 by H.E. Peterson (then at Continental Can Company, Inc., Chicago) when he added it to insecticides of the P-12/kerosene type to achieve a suitably fine particled spray pattern, while keeping the pressure at or below 25 psig at 70°F (172 pKa at 21.1°C) in order to meet certain interstate commerce regulations in force at that time.

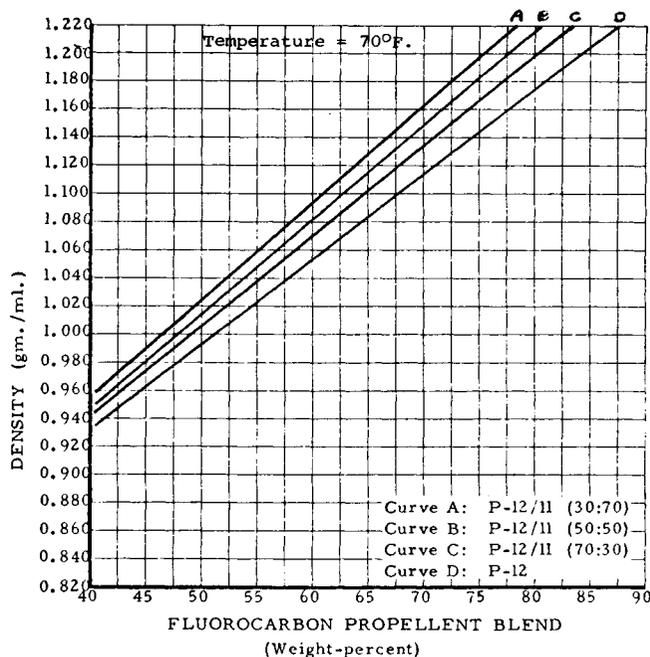


Figure 5. Density of CFC-11/12 Mixtures with Ethanol

When added to P-12 formulas, P-11 also adds solvency and density. Being non-flammable, it reduces the flammability of aerosols whenever it replaces a portion of the concentrate.

It is commonly purchased as a prepared blend with P-12. A format has developed for the nomenclature of these particular blends; for example a combination of 60% P-12 and 40% P-11 would be stated: P-12/11 (60:40). The "12" always appears first.

Unlike P-12, which resists hydrolysis in aqueous solutions or dispersions below about pH 12.5, P-11 is readily hydrolysed under most conditions. At least three unrelated reactions are involved, leading to such products as P-21 (CHCl_2F), itself unstable in alkaline media, P-112 ($\text{CCl}_2\text{F.CCl}_2\text{F}$), CO_2 , HCl and HF . It may be stable in acidic or neutral systems if held in glass or plastic. But in aerosol cans, even double lined tinsplate variables, the presence of tiny traces of iron, tin and copper is often sufficient to cause a 10,000-fold increase in hydrolytic decomposition rate. By adding about 0.1% nitromethane to the formula, these reactions are almost 100% eliminated. Nitromethane likewise inhibits P-11 hydrolysis in hydroalcoholic solutions containing at least as high as 98% pure ethanol. In essentially anhydrous alcohol solutions, P-11 can react with the ethanol in a free radical mechanism to produce

TABLE VIII
Amounts of Phosgene (mg) Formed by the Pyrolysis of One Gram of Propellents

Temperature		P-11 Against		P-12 Against		Methylene Chloride Against	
°F	°C	Steel	Quartz	Steel	Quartz	Steel	Quartz
392	200	0	0	0	0	0.007	0.0005
572	300	0	0	0	0	0.06	0.0025
752	400	0	0	0	0	1.3	0.0035
932	500	0	0	0	0	10.4	0.0440
1112	600	0	0	0	0	—	1.60
1292	700	0.002	0	0	0	—	9.3
1472	800	0.013	0	0.001	0	—	22.0
1652	900	0.21	0.07	0.009	0	—	18.
1832	1000	19.	7.04	0.13	0.002	—	18.

Propellant/air mixtures held about four hours in steel or quartz tubes.

Phosgene is a product of only one of several known reactions.

TABLE IX
Pressure of Pure Fluorocarbon Propellents at Various Temperatures

Temperature		P-11	P-12	P-21	P-22	P-113	P-114	P-115
40°F 4°C		-7.8	37.0	-2.2	68.3	-12.1	0.5	58.3
50°F 10°C		-5.9	46.7	0.7	85.4	-11.2	4.0	72.1
60°F 16°C		-3.9	57.7	4.3	104.4	-10.4	8.1	88.2
70°F 21°C		-1.3	70.2	8.6	123.3	-9.3	12.9	104.9
80°F 27°C		1.6	84.2	13.3	145	-8.0	18.3	123.7
90°F 32°C		5.0	99.8	19.4	168	-6.1	24.6	143
100°F 38°C		8.9	117.1	25.7	193	-4.4	31.7	166
110°F 43°C		13.4	136			-2.0	39.7	189
120°F 49°C		18.5	158	41.0	255	0.7	48.7	216
130°F 54°C		24.3	181			3.7	58.8	252
140°F 60°C		30.8	207	61.2	340	7.2	70.1	291
150°F 66°C		38.2	235			11.0	82.0	335
160°F 71°C		46.3	265	85.0	343	16.1	95.3	376
170°F 77°C		55.2	297			21.6	110.0	422

TABLE X
Pressure of P-12/P-11 Blends at Various Temperatures

Composition		Temperature					
P-12	P-11	40°F 4°C	70°F 21°C	100°F 38°C	130°F 54°C	160°F 71°C	
100%	0%	37.0	70.2	117	181	265	
90%	10%	33.0	63.9	107	167	244	
80%	20%	29.0	57.3	97.3	151	223	
70%	30%	25.0	50.8	87.3	136	202	
60%	40%	21.0	44.2	77.2	121	180	
50%	50%	16.9	37.5	67.1	107	158	
40%	60%	12.6	30.5	56.8	91.9	137	
30%	70%	8.0	23.0	45.9	76.3	117	
20%	80%	2.9	15.3	34.2	60.1	94.6	
10%	90%	-2.7	7.1	21.9	42.8	71.3	
0%	100%	-8.7	-1.3	8.9	24.3	46.3	

Pressures in Table IX and X are noted in psig. To convert to kPa multiply by 6.895.

P-21 (CHCl_2F), acetaldehyde ($\text{CH}_3\cdot\text{CHO}$) and HCl . Nitromethane can again function as an effective inhibitor. In commercial products such as hair sprays, alcoholysis rarely occurs, but when it does the results are disastrous. The rarity is due to the presence of other ingredients, which either act to destroy traces of peroxide free radical reaction initiators or else exert direct chain-breaking effects of their own. Recognizing the beneficial effects of nitromethane, several CFC manufacturers have offered a blend known as P-11S to interested customers. It consists of a mixture of 99.7% ethanol and 0.3% nitromethane, and is designed to give a 0.1% level of the inhibitor in the average ethanol-type aerosol product. The "S" stands for *stabilized*.

P-11 should never be used in conjunction with anhydrous ethanol formulations in aluminum cans, since here a curious reaction may occur, producing P-21 (CHCl_2F), acetyl chloride ($\text{CH}_3\cdot\text{COCl}$) and H_2 . The acetyl chloride will promptly ruin the formulation and the nascent hydrogen will rupture the dispenser unless it can penetrate the seal rapidly enough to dissipate before creating intolerable pressures.

From time to time the CFCs have been blamed for excessive rusting of steel furnace surfaces. Tests have shown that P-12 does not react with steel or iron below about 1450°F (790°C) and P-11 fails to react below about 1220°F (660°C). These temperatures are readily

attained in the combustion area, but not outside this zone. Thus, some rusting of the steel may take place, where it is in contact with the flames, and this rate of oxidation may increase if traces of P-11 or P-12 are present in the furnace air intake, provided it is not supplied from outside the house. A more important consideration is methylene chloride, which can attack steel at temperatures at least as low as about 360°F (182°C). Several reactions occur, and products include phosgene (COCl_2), HCl , HF and CO_2 . The acid fumes attack the steel, forming divalent halides, which are then hydrolytically oxidized to iron (III) oxide, or rust. Rust accumulations on the heated exterior surfaces of the furnace are highly visible and have caused the bulk of field complaints and bad press. The generation of phosgene (COCl_2) by pyrolysis of P-11, P-12 and methylene chloride is shown in Table VIII.

When P-11, P-12 and particularly methylene chloride or 1,1,1-trichloroethane are burned, such as by the ignition of an aerosol spray, significant quantities of phosgene (COCl_2) carbon oxychlorofluoride (COCIF) and related compounds are formed. The phosgene (MAC = 50 ppb) has never proved fatal, but can cause nasal irritation, a burning numbness in the lungs and various stages of diarrhea. The accompanying fumes of HCl and (particularly) HF cause similar irritations and also attack metal surfaces. For these reasons, flame pro-

TABLE XI
Pressure of P-12/P-114 Blends at Various Temperatures

Composition		Temperature									
P-12	P-114	40°F	4°C	70°F	21°C	100°F	38°C	130°F	54°C	160°F	71°C
100%	0%	37.0		70.2		117		181		265	
90%	10%	34.2		65.7		110		172		250	
80%	20%	31.3		61.1		104		162		236	
70%	30%	28.1		56.1		96.3		150		221	
60%	40%	25.1		51.0		88.6		139		205	
50%	50%	21.5		45.6		80.3		127		187	
40%	60%	17.8		39.9		71.8		115		172	
30%	70%	14.1		33.6		62.5		102		155	
20%	80%	9.9		27.2		52.5		87.8		136	
10%	90%	5.2		20.2		42.2		73.6		116	
0%	100%	0.5		12.9		31.7		58.8		95.3	

Pressures are noted in psig. To convert to kPa multiply by 6.895.

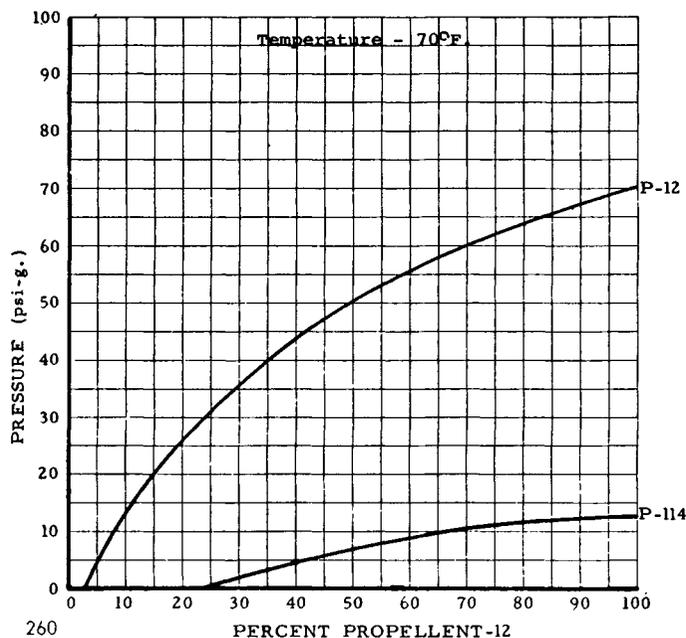


Figure 6. Pressure of P-12/Ethanol and P-114 Ethanol Mixtures

jection tests, the closed drum test and other combustion type studies should always be conducted in a well ventilated hood.

P-114 is the third most commonly used propellant; also one of the more highly fluorinated ones, since it contains 44.4% fluorine. Because of this it exhibits outstanding chemical, hydrolytic and thermal stability, as well as a very low odor level. Its low pressure has made it especially interesting as a propellant for glass aerosols, either straight or blended with P-12.

The pressure of various CFC propellents is compared with temperature in Table IX.

In addition, since P-12/11 and P-12/114 are blended very commonly to achieve special properties, the pressures of respective blends are shown at various temperatures in Table X and XI, respectively.

P-114 is a very poor solvent. About 78.7% P-114 even 95v% ethanol becomes immiscible at 70°F (21.1°C). The corresponding value for P-12 is 91.1%, and for P-11 it is 100.0%. The more highly fluorinated CFCs and CFs are even poorer solvents in general. Propellents such as P-115 and P-C318 are among the poorest solvents known.

P-114 is actually a commercial mixture of about 92% sym, dichlorotetrafluoroethane (CC1F₂·CCIF₂) and 8% 1,1-dichloro-1,2,2,2-tetrafluoroethane

(CCl₂F·CF₃). The second isomer, technically known as P-114a, boils only 0.6°F (0.3°C) away from the first and has virtually identical properties.

Throughout the world more P-114 is used for cologne and perfume sprays than any other application. A comparison of old and new formulations is shown in Table XII.

The hydrocarbon version is used only in the U.S.A., as a result of the CFC ban. When fragrance products are packaged in aluminum tubes instead of glass or coated glass there is no further need to limit pressures, and so formulas much higher in P-12 content are used. The pressure of various P-12, P-114 and anhydrous ethanol compositions is shown in Figure 6.

The higher and lower fluorine analogs of P-114 are identified as P-115 and P-113, respectively. Both have been used in aerosol formulations to some extent. P-115 is a rather high pressure fluid having poor solubility in both water and alcohol, as well as many oils. It disperses well, and this, coupled with its certification as a food-approved propellant, has led to its major use, as an adjuvant propellant for whipped toppings. By adding it to nitrous oxide or carbon dioxide, using a special system, the mixture can be used as a food propellant for puffed products, giving them more stability in the foamed stage and also allowing the last portion of the dispenser to dispense product that is not overly dense or runny, as would be the case for the compressed gas propellents alone. One interesting application has been for a chocolate ice cream topping. Without P-115, at about 1% of the total formula, the puff of product slowly lost its micelle structure at the surface, becoming progressively darker. This was very noticeable when the puff was touched with a spoon, exposing the much

TABLE XII

Glass Cologne and Perfume Aerosol Formulations

Ingredients	U.S.A.: Europe:	1952-1960	1091-1977 1961-1981	1978-1981 Future*
Perfume Oil		3**	3**	3**
Ethanol (Anhydrous)		37	—	—
Ethanol (95v%)		—	57	—
Ethanol (90v%)		—	—	77
P-114		60	36	—
P-12		—	4	—
Propane A108		—	—	5
n-Butane A17		—	—	15

*Dimethyl ether may also be used.

**This ingredient varies widely, and may go up to 12% or more in the case of perfume sprays.

lighter interior area. The stabilizing effect of the P-115 corrected the problem. It also allowed more product to be filled into a given can size, while still preventing any serious runniness or dense foam problems at the end of the can.

P-113 is not a true propellant, but rather a non-flammable, volatile solvent. It has been used as a specialty cleaner for electronic and television equipment, as a super-pure solvent for medical adhesives and as a component of colloidal Teflon dispersion-based aerosol dry lubricant sprays. Its density of nearly 1.6g/ml has helped keep the Teflon in suspension. The pressures of P-113, P-114 and P-115 at various temperatures are shown in Figure 7.

During the 1960s E.I. du Pont de Nemours & Co. developed Freon Food Propellant C-318 (perfluorocyclobutane, C_4F_8) specifically for use in food aerosol products. That was a time when there was a great deal of optimism about the possibility of expanding aerosols into the food specialties area, which unfortunately did not occur. Like P-115, P-C-318 helped produce more

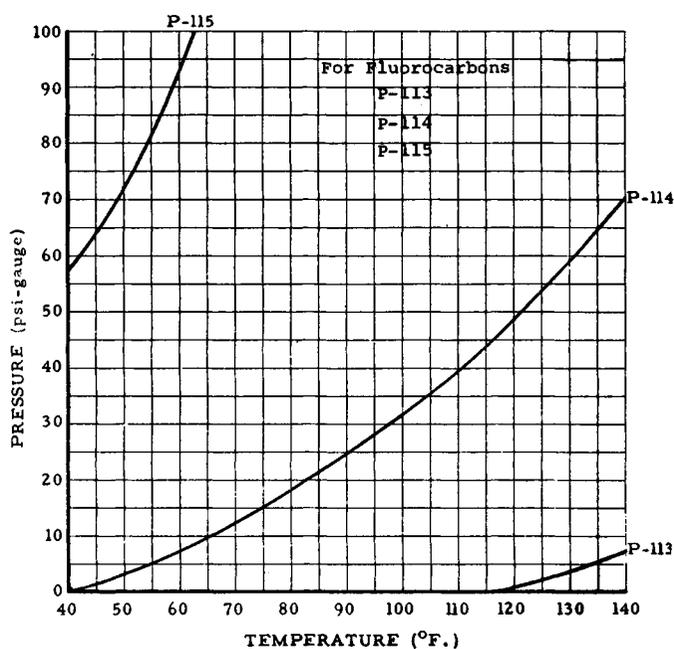


Figure 7. Vapor Pressure vs Temperature for Fluorocarbons P-113, P-114 and P-115

TABLE XIII

Physical Properties of Fluorinated Hydrocarbon Propellents (Uncommon Types)

	P-13	P-23	P-116	P-132a	P-133	P-227a	P-218	P-3110	C-318
Formula	$CClF_3$	CHF_3	C_2F_6	$CHCl_2CHF_2$	CH_2ClCF_3	C_3HF_7	C_3F_8	C_4F_{10}	C_4F_8
Molecular Weight	104.4	70.0	137.9	146.9	118.5	170.1	188.1	238.1	200.0
Boiling Point (°F)	-114.6	-115.7	-108.8	-136.1	41.8	-15.5	-38.0	28.4	21.5
Freezing Point (°F)	-294.	-247.7		-149.1	-158.	-258.	-297.	-121.	-42.5
Pressure (psi-g. at 70°F)	456.	603.	430.	- 11.4	11.3	65.3			25.4
Pressure (psi-g. at 130°F)	—	—	—	-1.8	56.1	178.			92.0
Density (gm./ml. at 70°F)				1.492	1.344		1.29	1.30	1.515
Density (gm./ml. at 130°F)									9.30
Vapor Density at B.P. (gm./l.)	7.01			4.66	91.	1.0	0.5	0.5	0.5
Water Solubility (ml./100 gm.)*	2.20	35.1	1.5	751.					5.1
Kauri-Butanol Number									5.64
Solubility Parameter						0.005	0.001	0.001	0.0003
Hydrolysis in Water (gm./yr.)**	0.005	0.005	0.005		0.010	0.005	0.002	0.002	0.002
Hydrolysis in 1% Na_2CO_3 (g/yr)**			0.010						
Hydrolysis in Water with Steel Strips Present (gm./yr.)**			0.05		0.06	0.04	0.005	0.040	
Flammability Limits in Air v%	none	none	none	none	none	none	none	none	none

*At one atmosphere and 77°F.

**Values expressed as grams HCl/liter of propellant/year, at 68°F when solutions of approximately 25% Propellant, 25% Water and 50% Isopropanol are stored in ampules.

stable foam structures and inhibited runniness and other problems when cans were nearly empty. One of the major incentives was to allow the marketing of whipped cream topping cans that were 70v% to 80v% full of product, instead of the 50v% standard that was developed out of concern for the runniness problem. However, when these new, more completely filled dispensers appeared on the market they were shunned by the consumer because of the higher price being charged for cans that seemed to be the same size as before. Eventually, sales of both food-grade propellents dwindled and have been almost discontinued. This is a sad commentary, considering the many millions of dollars spent in attaining their food-approved status.

The properties of FP-C318 (as it is often identified) are given in Table XIII (Page 329), along with those of eight other CFCs and FCs that are too uncommon in aerosols to mention here.

The Alternate CFC and FC Propellents

In the U.S.A. the virtual unavailability of the saturated (fully halogenated) CFC propellents, due to the regulatory ban of 1978, has led to a concerted search for other propellents. The hydrocarbons have major flammability and minor solvency problems, and the compressed gases, such as CO₂ and N₂O, have excess pressure, which limits their use to coarse spray products containing 6% or less of propellent. These deficiencies spurred research on propellents that seemed to offer either no or moderate flammability, better solvency, reasonable pressures, low toxicity and (of course) relatively low prices. One early combination seemed to be mixtures of P-21 and P-22, covering a pressure range of 8 to 123 psig at 70°F (55 to 845 kPa at 21.1°C), but toxicity studies initiated about 1976 quickly showed problems. The P-21 was considered toxic. Inhalation of 0.1% in air (6 hr daily, 5 days/week x 13 weeks) caused liver damage and excess mortality in the rat, although not in dogs. In addition, inhalation of 1% in air by pregnant rats (6 hr daily x 10 exposures—days 6-15 of 21-day gestation) was embryotoxic in 15 of 25 rats. The P-22 was considered possibly very slightly mutagenic and teratogenic. The Bruce Ames test for mutagenicity in *Salmonella typhimurium* bacteria was positive, and a standard teratogenicity test involving inhalation of various concentrations (100 to 50,000 ppm) by pregnant rats (6 hr daily x 10 exposures) showed an 0.45% incidence of microphthalmia (smaller than normal eyes) or anophthalmia (no eyes) in the fetuses. The

statistical significance of this finding, particularly below the highest level of 50,000 ppm or 5%, remains questionable. Comparably exposed rabbits were not affected. During 1979, results from du Pont's Haskell Laboratory and from a large scale European teratology study have suggested that no teratogenic hazard for women exists at the OSHA workplace standard of 1000 ppm (v/v). A chronic two-year inhalation study has been conducted on mammals in England. As of January 1, 1982 only the summary results have been made available. They are very encouraging, showing that P-22 is not a teratogen or mutagen at any reasonable exposure level. In fact, there are no effects until long-term exposures at 10,000 ppm or higher are involved. Tumors of the salivary gland were found at 50,000 ppm, long-term, but not at 10,000 ppm.

Once the results of the two-year (lifetime) study can be assessed fully it is highly likely that P-22 will be approved and offered for sale as an aerosol propellent in the U.S.A. and Europe. Aside from being non-flammable it has other interesting properties. For example, below 34% P-22, its mixtures with ethanol have lower pressures than corresponding P-12/ethanol blends. A blend of 30% P-22 and 70% ethanol has been suggested for glass aerosols; the pressure is 24 psig at 70°F (164 kPa at 21.1°C).

As of early 1982 the only alternate fluorocarbon propellent in commercial use for aerosol applications was P-152a (CH₃.CHF₂). The physical properties are described in Table VIII. It is chemically very stable, and since it contains no chlorine or bromine it is not involved in the CFC/ozone controversy and is free from any regulatory restrictions. It is a rather ideal propellent, except that it is flammable and some seven times as costly as the competing hydrocarbons. The molecular configuration makes P-152a dipolar and a

TABLE XIV
Borderline Solubility Compositions of P-152a, Ethanol and Water

Ingredients	Compositions			
	A	B	C	D
Ethanol (100%)	30	45	47.7	45
Water	10	20	27.3	40
P-152a	60	35	25.0	15

The addition of a tiny amount of either water or P-152a to any of these formulas will cause phase separation. In every case the air-free pressure is 62 psig at 70°F (427 kPa at 21.1°C).

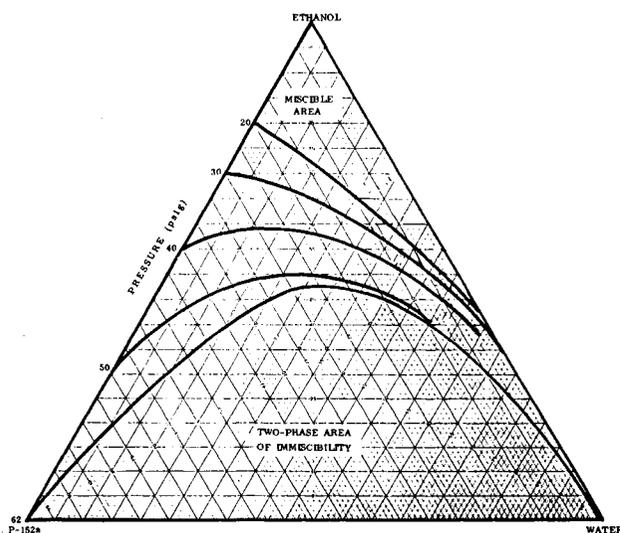


Figure 8. Pressure and Phase Diagram for Blends of Ethanol, Water and P-152a

Pressure isobars are on an air free basis. Temperature is 70°F (21.1°C)

good solvent for both apolar and other dipolar liquids. It is soluble in water to the extent of 0.28% at atmospheric pressure and 77°F (25°C), and to a level of several times that (1.66%) under its own vapor pressure at the same temperature. It is soluble in all proportions in a solution of 47.7% ethanol in water, at 77°F (25°C). Several borderline solubility compositions for the Ethanol/water/P-152a system are shown in Table XIV and the overall picture in Figure 8.

Although P-152a is technically flammable, the pure propellant spray cannot be ignited in the flame projection test, and the lower explosion limit (LEL) is 3.9v% minimum in air, compared with 1.6v% minimum in air for isobutane. Actually, P-152a/air mixtures are about a hundred times more difficult to ignite than hydrocarbon/air blends, but this fact has practical importance only when spark sources are used for mixtures that are fairly close to the LEL or UEL compositions. Approximately 32% of either P-12 or P-114 would have to be added to P-152a to make the overall composition non-flammable.

Perhaps the single largest product application of P-152a in the U.S.A. is the indoor fogger, due principally to the development of such formulations by a single filling firm. This product is designed to be placed in the center of a room or area to be cleared of both

crawling and flying insects, actuated using a latch-down valve design, and sprayed until the can is empty. After three or four hours, during which the toxicants will presumably have penetrated into just about every nook and cranny and have killed the insect population, the area is reentered and aired out. This type of product poses a set of new constraints on the flammability of the aerosol. Instead of spraying just a few grams, as in the case of most insecticides and other aerosol products, the indoor fogger sprays from about 150 to 200 grams into a closed area at one fell swoop. This new and different dispensing mode caused marketers to worry about flammability from a total use standpoint. If the can were to be actuated near a floor furnace, or in a confined area containing a stove or hot water pilot light, could the spray cause an explosion and fire? To minimize that possibility, formulations were developed according to two schools of thought:

Ingredients	P-152a Type	Propane Type
Petroleum Distillate and Toxicants	8%	8%
1,1,1-Trichloroethane	48%	60%
Methylene Chloride	20%	20%
P-152a	24%	—
Propane A108	—	12%

The propane type is much less expensive, but is it more flammable? Considering the 1,1,1-trichloroethane as neutral in terms of relative flammability, one must decide if 24% of a somewhat flammable propellant is more or less hazardous than 12% of a very flammable one. Closed drum tests indicate the two formulas are extremely comparable, but there may be other criteria, such as vapor density and diffusion rate, that must be considered for a total answer.

The same exercise has been applied to a choice between P-152a and hydrocarbon propellents in the case of plain glass aerosols, which could discharge the entire content upon breakage. The hydrocarbons seem to be preferred strongly in this case, perhaps because the package size is so small (normally 20 g or less), and there would be someone there to cope with a small fire if it should get started.

The final use of P-152a is where its solvent properties are required. In one instance, a medical concentrate high in non-ionic surfactant content could not dissolve

enough isobutane to produce a satisfactory spray. Taking 50 g of concentrate, phase separation took place when over 21 g of isobutane was added. The final formulation consisted of 50 g of concentrate, 25 g of isobutane and 25 g of P-152a. It produced the desired spray pattern. In this case, the P-152a acted as a co-solvent, propellant and pressure booster. Pressure enhancement occurred as a result of its azeotropic properties.

In the second case, a surfactant solution designed to provide a fairly unstable sprayed foam was pressurized with a combination of 1 g of isobutane and 4 g of nitrous oxide. The hydrocarbon enhanced foam stability, while the nitrous oxide increased the breaking rate. The combination gave the degree of instability that was desired. As it turned out, these propellents were sufficiently hard to add accurately to the dispenser, that production rates were very poor. In addition, the last portions of the product were delivered with poor foamability, due to the depletion of propellant in the concentrate as the head space increased in volume. All these problems were solved when about 2.5% P-152a and 0.5% hydrocarbon A63 (isobutane/propane) were premixed and added as the 3.0% total propellant. However, the cost did increase to some extent.

As a final example, P-152a (along with a small percentage of ethanol) has been used in the formulation of quick-breaking foam products. In the case of the

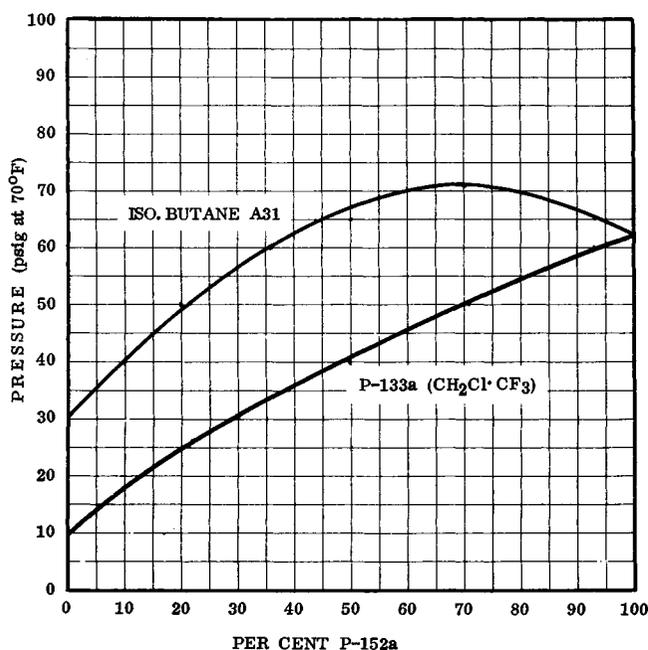


Figure 9. Pressure for Blends of P-152a/Isobutane and P-152a/P-133a. Temperature: 70°F

saturated CFCs and hydrocarbon propellents, much higher levels of ethanol would be needed; perhaps more than would be wanted to develop the optimum formulation.

Rather interestingly, preliminary studies have shown that dimethylether (DME) can probably replace P-152a in each of these examples, although its much greater solubility would necessitate using less of it in the case of quicker breaking and less stable foam structures. It is currently priced at about a third that of P-152a, and this merely adds another incentive.

P-152a exhibits a fairly rare property for an aerosol propellant: it forms azeotropic blends with essentially non-polar propellents. Thus, its mixture with 21% propane exhibits a pressure of 122 psig at 70°F (841 kPa at 21.1°C) and the mixture with 29% isobutane has a pressure of 71 psig at 70°F (490 kPa at 21.1°C). These are the azeotropic maxima, substantially higher than the pressure of any of the pure propellents. On the other hand, with a polar substance such as P-133a (CH₂Cl·CF₃) a perfectly normal pressure-composition curve is formed. The isobutane and P-133a curves with P-152a are illustrated in Figure 9.

The last commercially significant propellant in this category is P-142b. Like 152a, this fluid was offered to the aerosol industry over thirty years ago. P-152a was known as P-100 and P-142b was identified as P-101 in those early days. Neither enjoyed any significant aerosol applications, perhaps because of their flammability and somewhat higher cost.

P-142b (CH₃·CClF₂) is a CFC and thus must be considered in terms of the ozone question. No regulatory sanctions have been imposed yet, but they are anticipated from a reading of the EPA's ANPR of October 7, 1980, discussed earlier in this chapter. The calculated tropospheric lifetime is 24 years (compared with P-11 at about 91 years) and the ozone depletion relative to P-11 is about 0.09. As a result, approximately 20 pounds of P-142b would have the same predicted effect upon ozone as one pound of P-11. (The figure for P-22 is 34 pounds.)

Several observers feel that the regulatory situation being considered by the EPA against all uses of CFCs, including the permit-pound concept, probably will not materialize due to business and political opposition. Firms considering the use of P-142b should regard the CFC status as only a mild deterrent.

P-142b appears to have a satisfactory toxicological profile, despite an early Ames test result that classified

it tentatively as a very weak mutagen. It appears not to be a teratogen. For instance, pregnant rats inhaling up to 50,000 ppm P-142b in air, 6 hr daily for 10 days during mid-term exhibited no abnormalities in either mother or fetuses. A dominant lethal mutation study, where male rats were exposed to P-142b and then mated, showed no problems in the case of the offspring. The key test is a chronic mutagenic/carcinogenic study underway at Biodynamics Laboratories (Millstone, NJ) with completion set for late 1982. Mammals are exposed to 1,000, 10,000 and 20,000 ppm of P-142b in air for six hours per day. Interim results at six months and twelve months have not shown any ill-effects.

The toxicology picture thus far has encouraged at least one supplier to offer P-142b commercially in the U.S.A., another manufacturer has decided to await further data development before making it available for aerosol uses.

P-142b is made by reacting HF with 1,1,1-trichloroethane in the presence of selected catalysts and conditions. Despite the similarity between P-142b and P-152a, the latter is made by quite a different route, involving the addition to HF to acetylene. P-142b has a higher density and lower pressure than P-152a. Their properties are compared in Figure 10 and Figure 11.

P-142b is probably the most dipolar of the ethane-based propellents, except for P-143a ($\text{CH}_3\cdot\text{CF}_3$). Yet it is only about a third as soluble in water as P-152a and has a slightly lower solubility parameter. The departure from expected behavior is due probably to the larger size of the molecule.

P-142b is only slightly flammable, having flammability limits in air of 6.0 to 15.0v%. By the same test, a blend of 74% P-142b and 26% P-12 is non-flammable, although borderline, 66% P-12 is required to produce the same effect with P-152a. Both P-142b and P-152a are incapable of producing a flame extension when sprayed. They evaporate completely from flash point testers without giving any flash point or fire point.

At this time, due to the uncertain toxicological and regulatory situations, plus the fairly high price, P-142b is not used to any measurable extent in aerosols. In the past it has found a few applications in glass aerosols because it is a better solvent for perfume ingredients than P-114 (or the butanes), and has also been used in one or two quick-breaking foam products. One report suggests that the addition of a P-142b/propane propellant to shaving creams will result in richer foams, with a more pearl-like or satiny surface and texture. The defatting effect of P-142b would have to be evaluated carefully for such applications.

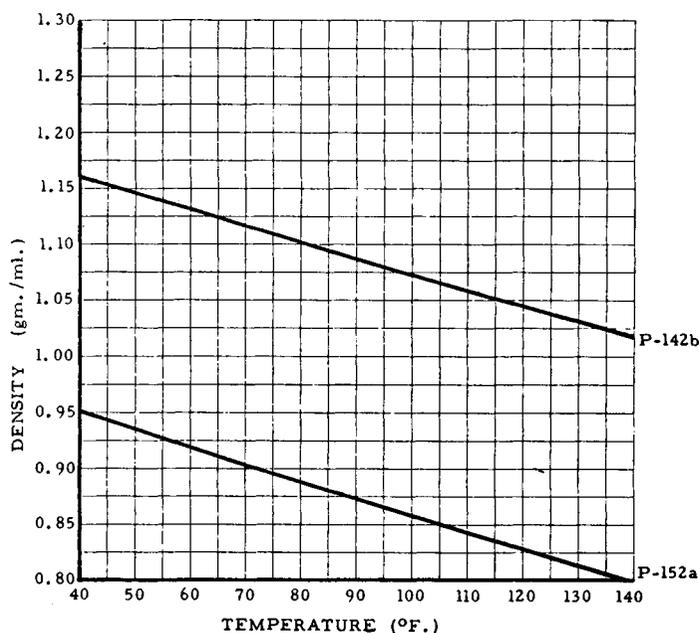


Figure 10. Density of P-142b and P-152a at Various Temperatures

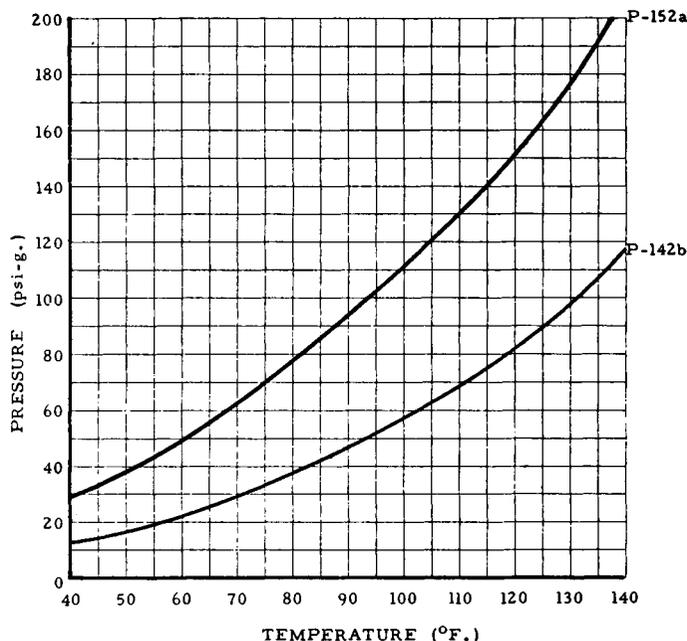


Figure 11. Pressure of P-142b and P-152a at Various Temperatures

The Bromochlorofluorocarbons and Bromofluorocarbons

These aeroform fluids can function as aerosol propellents but are not normally used as such, so their discussion is brief. There are about six or seven commercially available compounds, all under the trade-name of *Halon*, but only Halon 1301 (CF_3Br) by duPont and Halon 1211 (CF_2ClBr) by I.C.I. United States Inc. are of any real importance. They are used almost exclusively as fire extinguishing agents, breaking the combustion reaction chain and cooling the fire. Two major reaction chains are involved: free-radical and ionic. The major decomposition products are CO_2 , HBr , HCl (if Cl is present) and HF , but minor amounts of Br_2 (bromine), COBr_2 (carbonyl dibromide), COCl_2 (phosgene — if Cl is present), COF_2 (carbonyl difluoride) and carbonyl mixed halides are formed.

Although the Halons have not been implicated directly in the regulations relating to the CFC/ozone

controversy, the omission probably arises from their disassociation with aerosols in general. They are manufactured in more limited quantities than the major CFCs. Certain Halons are very susceptible to tropospheric reactions. For example, Halon 1211 in the presence of 400 ppm of moisture will hydrolyse and produce sufficient acid to perforate a tinfoil aerosol can within 24 hours. It would not be expected to survive hydrolysis in the troposphere to any extent, and may therefore be considered as non-threatening to stratospheric ozone.

The Halons have a wide pressure range, and blends have been used often. Combinations with P-12 and also CO_2 have been employed, mainly to increase the pressure of Halon 1211. The pressures and densities of selected Halons and blends are shown in Figure 12 and Figure 13.

The 20% P-12 and 80% Halon 1211 mixture is now used widely for smaller fire extinguishers outside the U.S.A. They may be found in cars, boats, garages, workshops, laboratories and in some houses. Some con-

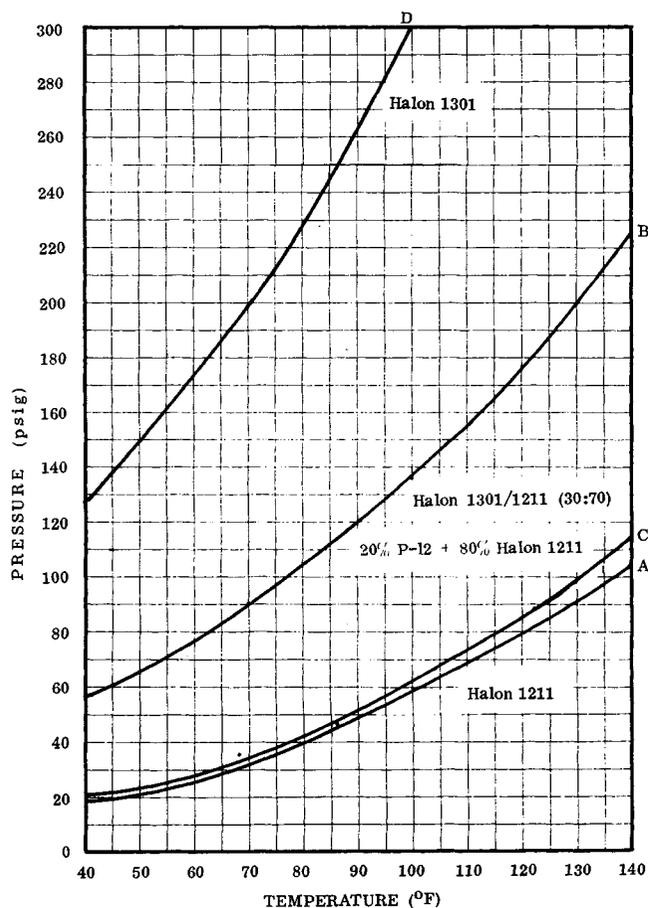


Figure 12. Pressure of Common Halons and Blends

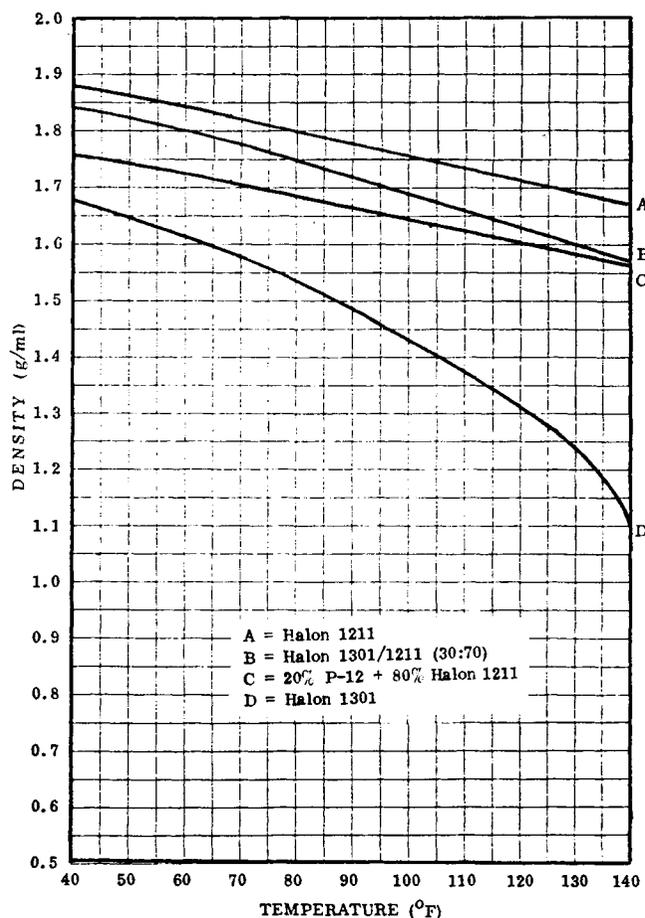


Figure 13. Density of Common Halons and Blends

tingency studies are being performed using a 16% P-22 and 84% Halon 1211 composition, in case sanctions against P-12 are increased.

On a practical basis, to sell a fire extinguisher in the U.S.A. one must obtain Underwriters Laboratories (UL) approval. This is an extremely complex, long and costly affair; so much so that no ordinary aerosol dispenser has yet been approved. One of the numerous test requirements involves the extinguishment of an n-heptane fire having a fuel surface of 1.0 sq. ft. (305 x 305 mm) at -40°F (-40°C). The relatively large, heavy-duty fire extinguishers, typically holding from 4 to 7 lbs. (1.8 to 3.2 kg), are formulated by adding sufficient CO₂ to Halon 1211 to generate a 70 psig minimum pressure at 70°F (483 kPa at 21.1°C) in order for the product to put out fires with an operating range of -40° to 120°F (-40°C to 49°C) minimum. Such products have a Class B fire rating and Class C electrical rating. They must have a small (patented) pressure gauge integral with the dispenser to assure that no CO₂ leakage has occurred, thus preventing proper operation at very low temperatures. The British Standards Institute, which is the equivalent of the UL in the United Kingdom, is not as strict, and for this reason aerosol fire extinguishers of the non-returnable type represent a significant portion of the aerosol business in that area. Similar situations apply over much of the rest of the world.

The toxicology of the Halons has been rather well defined. Once these substances are used to put out a fire, the noxious nature of the reaction products (typically at the 10 to 50 ppm level) will be sufficient to limit human exposure to both the unreacted Halon and its decomposition residues. One of the less common Halons is unique in that it has one of the most intense cardiac sensitization and arrhythmia profiles ever recorded. This is not a significant problem with the common Halon materials.

The Hydrocarbon Propellents

The hydrocarbon propellents became the dominant type worldwide during 1979. During that year and through at least 1982 these gases will have accounted for about 90% of all U.S.A. aerosol units, and for a requirement of about 300 million pounds per year (136 million kg/yr). In Canada about 82% of all aerosols contain hydrocarbon propellents, although sometimes in combination with CFC types. The figure is the result of a selective ban, directed at hair sprays, colognes and underarm products, since these accounted for the great

bulk of CFC sales in that country. Rather interestingly, the ban results only to "true propellent" uses; not to solvent or carrier uses. This tends to exempt P-11 and P-113 from consideration. As one result of this situation, the leading antiperspirant spray now uses a formulation consisting of about 10% concentrate, 65% P-11 and 25% hydrocarbons. It is considered superior to the straight hydrocarbon types since it does not inject so much acidic dust into the air during use. The liquid droplets of P-11 carry over 88% of the astringent aluminum chlorhydrate to the underarm area and then quickly evaporate. In contrast, the isobutane in straight hydrocarbon propellent types evaporates almost immediately upon release, leaving nothing but a bit of oily material (isopropyl myristate and/or volatile silicone) to carry the aluminum compound to the skin. As a result, only about 55% is actually transferred; the rest floats about as a dusty, irritating cloud in the air, to the aggravation of the user. This situation is further elucidated in Figure 14.

In Europe the use of CFCs also decreased substantially during the post Rowland-Molina period, and particularly during 1978-1982. After a review of the

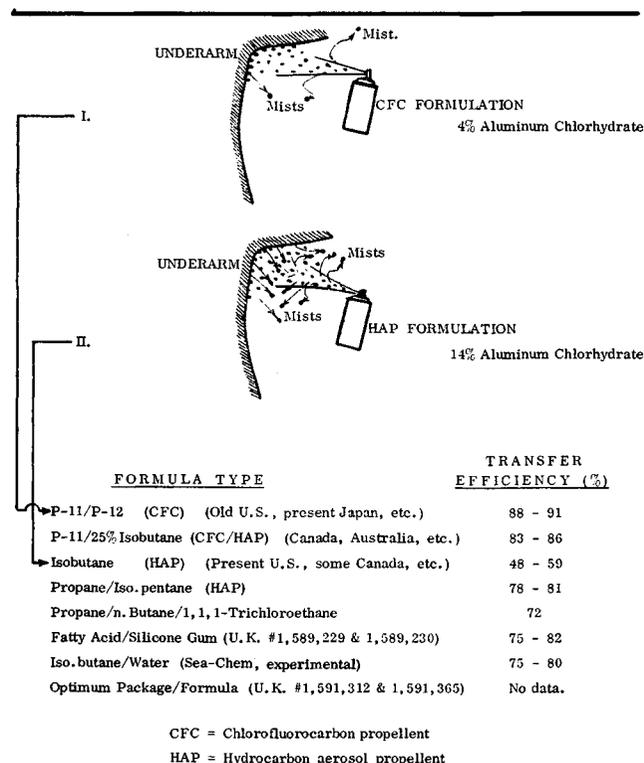


Figure 14. Anti-Perspirant Transfer Efficiency

CFC/ozone theories the EEC asked for a voluntary reduction of 30% in CFC aerosol uses by January, 1982, compared with the 1976 level, and promised a mandatory reduction if this was not accomplished. The reduction was in fact realized, although much more so in some countries than others, and the EEC has now recommended a continuing voluntary freeze at a level not to exceed 102% of the Jan. 1, 1982 figure. The results of a Metra, Ltd. survey of the 1979 propellant selections for various European countries are incorporated into Table XXV of the Aerosol Marketing chapter.

The 1982 usage level varies widely from country to country in Europe. For example, it extends from a level of about 70% of all aerosol units in France, where about 25% of their production is in 100% CFC type fragrance products, to only 2% in Norway and Sweden, where virtual bans on CFCs are in place. The usage level also varies widely from filler to filler, partly depending upon the filling facilities that are available. The data in Table XV illustrate the differences between the four largest filling installations in Switzerland, as well as the breakdown of uses between product categories.

From 1982 on, the European consumption of hydrocarbon propellents will increase further, as marketers

become more confident of the new formulas, and as fillers develop more sophisticated gassing facilities to handle these more economical gases.

In the U.S.A., isobutane is by far the most popular hydrocarbon propellant, accounting for about 70 to 75% of the total aerosol use of hydrocarbons. This is despite the fact that this gas accounts for only 4% of the composition of well-head LP-gas mixtures and is the most expensive of the common hydrocarbons. Propane occupies about a 15 to 20% market share, while n-butane has around a 10 to 15% share.

In other countries the use of hydrocarbon often depends upon what is available locally. For example, the natural gas fields in southern Australia yield a combination of approximately 60% propane and 40% butane that is refined and sold as is for most aerosol uses. If a higher or lower pressure propellant is needed, it is produced from the basic blend by distillation and sold at a modest premium.

About 20% of all the n-butane that goes into aerosols enters as a co-propellant, as a recognized ingredient in isobutane and (to a much lesser extent) in propane. In a similar fashion, co-propellents include up to about 3% ethane in propane and 3% isopentane in blends high in n-butane. The purified, Aerosol Grade propellents are specified to have a minimum purity of 95.0 w%, and this leaves ample room for the co-propellents as mentioned. For some aerosol products, such as paints, lacquers and certain industrial types, the use of purified (low-odor) Aerosol Grade hydrocarbons has been deemed unnecessary by many marketers. The Commercial Grade LP-gases are used instead. On the average, these compositions have a higher odor level and a broader pressure range than the Aerosol Grade gases, but they are also significantly less costly. As a general rule the Commercial Grade materials can be considered to have purities above about 90.0 w% for the individual gases, but specifications are tied more closely to pressure range than actual composition. Most of the Commercial Grade aerosol propellents are either propane or blends containing a substantial amount of propane. In early 1982 propane was selling at \$0.39 per gallon (\$0.10 per liter) and ethane at only \$0.21 per gallon (\$0.055 per liter). This price difference indicates the incentive for refineries to inject as much ethane into their Commercial Grade propane as possible, within the pressure limit of 224 psig at 100°F (1.54 MPa at 37.8°C) laid down by the American Petroleum Institute (API) and other groups. Whereas the pressure of Aero-

TABLE XV
*Aerosol Propellant Use Profile in Switzerland
(1977-1978)*

Filler	Product Mix	Propellant Usage	
		CFCs	HAPs
1.	All kinds of aerosol products	73%	27%
2.	Principally cosmetic items	82%	12%
3.	All kinds of aerosol products	82%	18%
4.	Only cosmetics	100%	0%

Product Group	Per Cent of Use (By Weight)		
	CFC Only	CFC/HAP	HAP Only
Cosmetics			
Hair Sprays	64.7	35.3	0.0
Underarm Products	90.4	3.2	6.4
Perfumes/Colognes	100.0	0.0	0.0
Others	12.6	10.1	79.3
House and Garden	7.9	36.4	55.7
Chemical/Technical	85.2	0.0	14.8
Paints and Lacquers	10.5	0.0	89.5
Pharmaceuticals and Veterinarian Items	88.5	7.6	3.9
Overall	47.2	16.0	36.8

Courtesy of Dr. Willi Roth - ASA

sol Grade propane is 114 psig at 70°F (786 kPa at 21.1°C) as a maximum, the pressure of the Commercial Grade material may get to 128 psig at 70°F (883 kPa at 21.1°C), as a result of an ethane content approaching 4.0%. Steps are underway to allow the introduction of even higher amounts of ethane. The presence of ethane is not a problem, except that it may act to elevate the pressure of the finished aerosol product. Ethane will provide a finer break-up of the spray than propane, but this is rarely a disadvantage within the limits involved in this case.

The LP-gases have natural origins, being extracted from both crude oil and natural gas supplies. U.S.A. natural gas contains an average of 25.9% ethane (1981 figure; dropping about 0.8% per year), 12% propane, 7% n-butane and 3.7% isobutane. The largest component of natural gas is methane, generally at over 50%. Smaller constituents include n-pentane, isopentane and the isomeric hexanes. Carbon dioxide is usually present. Finally, there are a large number of other compounds in the raw gas streams which are considered undesirable for aerosol applications, due to odor, reactivity or other factors. They include the unsaturated hydrocarbons, such as ethylene $\text{CH}_2\text{:CH}_2$, propylene $\text{CH}_3 \cdot \text{CH:CH}_2$, 1-butene $\text{CH}_2\text{:CH} \cdot \text{CH}_2 \cdot \text{CH}_3$, 2-butene $\text{CH}_3 \cdot \text{CH:CH} \cdot \text{CH}_3$, isobutylene $(\text{CH}_3)_2\text{C:CH}_2$, the pentenes, acetylene CH:CH , methyl acetylene $\text{CH}_3\text{C:CH}$, allene $\text{CH}_2\text{:C:CH}_2$ and butadiene $\text{CH}_2\text{:CH.CH:CH}_2$, as well as sulfur compounds; e.g. hydrogen sulfide H_2S , alkylthiols (formerly mercaptans) $\text{CH}_3\text{-SH}$, etc. and dialkyldisulfides R-S-S-R' . Moisture may also be present.

In any given well these individual components may vary quite widely. Some wells have had to be capped because the gas stream contained over 50% hydrogen sulfide and there was no practical way of using the product. Others are unusually rich in acetylene, which is an impurity difficult to remove. These particular wells are shunned by the firms who purify LP-gas into aerosol propellents. Finally, the ratio of n-butane to isobutane varies from about 80:20 to about 60:40, depending on the well. Wells with the higher stream contents of isobutane are preferred for aerosol purposes.

Despite the fact that only 0.1 percent of the U.S.A. propanes and butanes are directed to aerosol propellant applications, this segment amounts to sales of about \$70 million per year. About 58,000,000 gallons of raw feedstock are purified to Aerosol Grade materials, and an

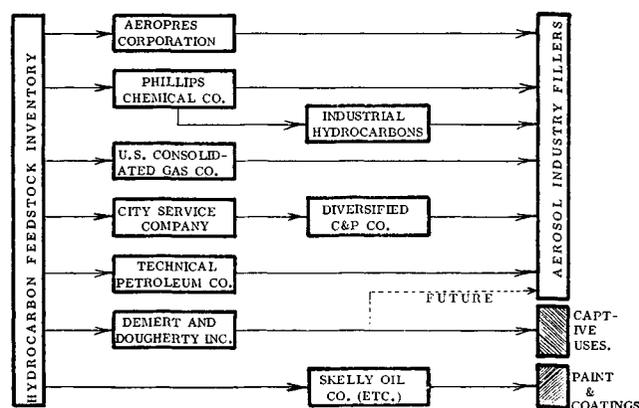


Figure 15. Refiners and Resellers of Aerosol Hydrocarbon Propellents

Two of the largest resellers of Aerosol Grade hydrocarbons in the U.S.A. and Canada are Diversified Chemicals and Industrial Hydrocarbons.

additional 11,000,000 gallons or so are sold directly to aerosol fillers as the Commercial Grade product. Six firms are currently engaged in the purification of one or more of the gases in the group consisting of propane, n-butane and isobutane. They are listed in Figure 15.

The Aeropres Division of Aeropres Corp., the Phillips Chemical Co. subsidiary of the Phillips Petroleum Co., the City Service Co. and the Technical Petroleum Co. are basic suppliers of Aerosol Grade hydrocarbons. They can provide this grade of propane, n-butane and isobutane, or virtually any mixture of these gas liquids. On the other hand, U.S.G.L., Inc. of the U.S. Consolidated Gas Co. can supply only isobutane. DeMert & Dougherty, Inc. is a Chicago area aerosol filler who installed a purification unit during 1980 and is willing to sell excess propane and n-butane.

There are several resellers of Aerosol Grade hydrocarbons in the U.S.A. and Canada. Two of the largest are Diversified Chemicals and Propellents Co. (Chicago area) and Industrial Hydrocarbons, Inc. (Los Angeles area). Diversified Chemicals and Propellents Co. provides their Aeron[®] gas liquids via seven distribution terminals across the U.S.A. and also does business in Canada. They are now installing their own propellant purification facilities. On the other hand, Industrial Hydrocarbons, Inc., sells Phillips 66's A-17[®] (n-butane), A-31[®] (isobutane), A-108[®] (propane) and blends primarily in the Western States. Both firms sell purified hydrocarbons for other purposes, and have business interests that include CFC applications, resale of methylene chloride, and so forth.

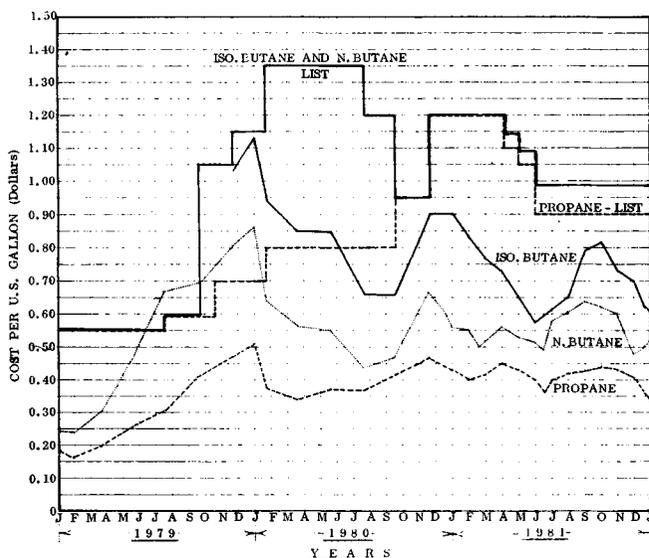


Figure 16. Field Grade and Aerosol Grade Prices of the Common Aerosol Hydrocarbon Propellents

Spot prices for Field Grade hydrocarbons are updated weekly. Prices for Conway, KS hydrocarbons are illustrated. Prices for Mt. Belvieu and Sarnia (Canada) gases are generally within $\pm 10\%$ of the Conway KS figures. They are for tankcars, f.o.b. source. List prices for Aerosol Grade materials are for tankcars, f.o.b. source.

For those aerosol paint fillers and others who may wish to purchase a Commercial Grade hydrocarbon propellant, there are sellers such as Phillips Petroleum Co. (out of the U.S. Industrial Chemical Co.'s plant in Tuscola, IL, for example), and Dome Petroleum Ltd. (Sarnia, Ontario, Canada) Terminals also exist at Conway, KA, Mont Belvieu, TX and other locations. This grade of propellant is also known as feedstock quality, fuel grade, and field grade. The prices are revised on a weekly basis. They are compared with the Aerosol Grade prices for propane, n-butane and isobutane in Figure 16.

The price of propane, n-butane and isobutane is affected by massive factors outside the realm of the aerosol industry. Natural gas is the major source for these gas liquids, and the extent to which it is needed for a myriad of other uses controls the cost. After the natural gas undergoes CO_2 -stripping, deethanization and other operations, the gas-processing plant uses a depropanizer unit to separate the propane, after which the isomeric butanes are separated in their turn. The remaining feed stock is distilled into relatively pure n-pentane, isopentane, hexanes and other light fractions according to need, but these are of limited interest to the aerosol formulator.

The mixed butanes may or may not be separated. They are very often used directly as components of liquefied petroleum gas (LPG) and synthetic natural gas (SNG). Starting in 1980 the mixed butanes (especially about 60% n-butane and 40% isobutane) began to be used along with propane in the formulation of certain purified, lower cost aerosol propellents. The blends had pressures in the range of about 24 to 70 psig at 70°F (165 to 483 kPa at 21.1°C) and were sold under such tradenames as Aeropin® (Aeropres) and Aerosol BIP® (Phillips). Their lower cost could be justified on the basis that the approximate \$0.10 to \$0.14 per gallon cost (depending on freight increment) of separating the butanes was saved; also, n-butane was less costly than isobutane, and this dictated a savings when compared with the usual isobutane/propane combinations.

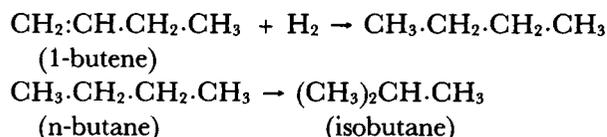
The domestic market for propane, n-butane and isobutane divides into three categories: fuel use, chemical use and net refinery use. The Aerosol Grade propellents were effectively taken out of the fuel classification through an action of the U.S. District Court for the Western District of Louisiana (June 15, 1981) which disallowed any Department of Energy regulation of these gas liquids as fuels. Thus they were, in effect, placed in the "chemical uses" category.

Regardless of how they are classified, the aerosol gases compete with fuel and other applications that require propane, n-butane and isobutane. These gas liquids in 1981 accounted for 67.3% of all ethylene production, leading to polyethylenes. About 3.6 billion pounds per year (1.6 million metric tons per year) of n-butane finds its way into chemicals: ethylene, acetic acid, maleic anhydride and butadiene, for example. Almost 1.0 billion pounds per year (0.44 million metric tons per year) of isobutane is used, mainly for tertiary butyl alcohol, but also for making propylene oxide via the Oxirane process, now owned by Arco. Propane will be the cheapest feedstock for steam crackers over the next decade.

The Oxirane process is of special interest to aerosol people. It involves a two-stage reaction mechanism, with isobutane, oxygen and propylene reacting to produce tertiary butyl hydroperoxide $(\text{CH}_3)_3\text{C}\cdot\text{O}\cdot\text{OH}$ as an intermediate, which then produces propylene oxide and also tertiary butyl alcohol as a co-product. The peroxide is characterized by having a strong, chlorine-like odor even at very low levels. It has been a sporadic site-generated contaminant in bulk tanks that hold isobutane or blends containing isobutane. It is particularly

likely to be produced in those tanks that may have previously contained P-11. The catalytic effect of iron/iron oxide and some moisture seems to allow the reaction to build up to at least 80 ppm. of the peroxide during ordinary outdoor storage conditions. To prevent a recurrence of the problem, many fillers empty, degas, and then sand-blast the affected bulk tank.

By far the major uses of the butanes are in the fuel area, in both heating gas and in gasolines. n-Butane is added directly to gasoline stocks to increase volatility for winter driving conditions. Isobutane is also added, to some extent, directly from the isomeric blend with n-butane, but mostly after alkylation. The butane alkylate has a high octane number and is much in demand. Anticipating periodic shortages of isobutane (and thus a higher price) Phillips, Tenneco and Marathon have all installed isomerization units to convert n-butane to isobutane. The large unit at Phillips' Borger, Texas refinery is used to convert mixtures of isobutane and n-butane to essentially 100% isobutane for aerosol purposes, among other applications. Unsaturated C₄ compounds (mainly isobutylene) are always present in the butanes feedstock, and by adding slightly over the stoichiometric amount of hydrogen, all these high odor impurities are converted to their saturated counterparts during the basic isomerization process. A typical reaction involving 1-butene would be as follows:



Phillips isobutane, made by this process, is unique in that it has much less than 1 ppm. of remaining unsaturates, whereas the industry standard for Aerosol

Grade gases is 10 ppm. maximum. Butane samples from other countries have been examined with the finding that they sometimes contain as much as 475 ppm. of these odorous and relatively reactive impurities.

Purification of Field Grade Propane, n-Butane and Isobutane

Field grade hydrocarbons suitable for rectification into Aerosol Grade propellents generally contain at least 95% w% of the primary hydrocarbon ingredient and have 70°F (21.1°C) pressures in the stipulated range for the final product, as shown in Table XVI.

Maintaining the pressure specification is particularly difficult in the case of propane. The absolutely pure compound has a pressure of 109.3 psig at 70°F (754 kPa at 21.1°C), but each 1% of ethane that is added increases the pressure by 3.9 psi (27 kPa). Introducing butanes to propane does very little to depress the pressure within the narrow limits that can be added. Rejection or blending with lower pressure propane are the only realistic solutions.

The purification of field grade stocks consists of the strong reduction or removal of active and odorous unsaturates and sulfur compounds, plus water. The total content of these ingredients is in the range of about 0.005 to 0.200%, with an average of about 0.015%, although the figures vary widely between sources and even within a given source, measured at different times. Two pipeline supply sources are known to vary in acetylene content from below 0.0001% to above 0.2200%. This can be a serious affair, because this impurity is very difficult to remove by passing the feedstock through absorbent solids.

A rather typical analysis profile of the in-plant feed, field-grade propane, field grade isobutane and field grade n-butane streams at Dome Petroleum Ltd.'s

TABLE XVI

Pressure Specifications for Aerosol Grade Hydrocarbon Propellents

Temperature = 70°F (21°C)

Hydrocarbon	Aeropres	De Mert & Dougherty	Diversified	Technical	Phillips
Propane A-1-8	110 ± 4	123 (max.)	108 ± 3	110 ± 4	108 ± 3 psig
Isobutane A-31	31 ± 2	—	31 ± 2	31 ± 2	31 ± 2 psig
n-Butane A-17	17 ± 2	17 (min.)	17 ± 2	17 ± 2	17 ± 2 psig

Note: At an industry meeting in 1979 with representatives from five suppliers or resellers present, typical properties of Aerosol Grade hydrocarbons were agreed upon as: propane 108 ± 6, isobutane 31 ± 2 and n-butane 17 ± 2 psig at 70°F. These were later printed in an industry publication.

“National Gasoline Plant” at Sarnia, Canada is given in Table XVII.

Not shown is the condensate stream, composed of about 25% n-pentane, 25% isopentane, 50% hexanes and higher, and about two-thirds of the C₄ unsaturate content of the in-plant feedstock.

Several methods are available for the removal of unsaturates, sulfur compounds and water. One procedure, used little in the U.S.A. but known in other parts of the world, involves the ambient temperature reaction of these impurities with 99% sulfuric acid. Propylene absorbs to give a series of polymers, plus some propyl hydrogen sulfate that yields isopropanol when hydrolyzed. Isobutane absorbs even more easily, to give 2,4,4-trimethylpentene-1 and many other polymers, plus some tertiary butyl hydrogen sulfate that produces tertiary butyl alcohol on the addition of water. This alcohol has a strong camphor type odor and may contaminate the hydrocarbon with this odor unless washed thoroughly with water. Butene-1 and butene-2 are polymerized to some extent and also yield secondary butyl alcohol on the addition of water. Acetylene is not polymerized by sulfuric acid, but yields acetaldehyde CH₃.CHO and crotonaldehyde CH₃.CH:CH.CHO instead. Hydrogen sulfide, alkythiols and alkydisulfides are oxidized by sulfuric acid, giving sulfur dioxide, monosulfoxides and monosulfones as illustrative of the large variety of possibilities. After the acid treatment the cleaned gas liquids are scrubbed through a Raschig ring column of 10% sodium hydroxide, followed by a column containing clean water. At a typical operating temper-

ature of 60°F (15.6°C) propane dissolves 129 ppm. of water and the butanes dissolve only about 54 ppm. This means that the usual reduction to the specification of 25 ppm. water (maximum) can be accomplished readily with solid drying agents. If the butanes are below 40°F (4.4°C) no desiccation is necessary; only entrapment of water droplets with aluminum turnings or some similar hydrophilic maze-like material. Optionally, the finished gas stream can be further “polished” by passing it through a granular type of activated carbon, such as Darco S-51, then through a very fine filtration unit and into a storage tank.

In the U.S.A. the sulfuric acid purification process is used generally only if unsaturate levels are about 0.25 to 1.00%, which is fairly rare, or if sulfur compound levels are excessive. Even then, it is only a preliminary purification step, with the final process involving absorption of contaminants by means of activated carbon and zeolyte (molecular sieve) mixtures. A basic sketch of such a system is shown in Figure 17, for the purification of field grade isobutane.

This system can be used for other propellant gas liquids, or expanded to simultaneously run other hydrocarbons by adding storage tanks, piping and purification towers.

A suggested procedure involves the fairly rapid (high-stream) passage of the gas liquid through a preliminary tower containing trays of activated carbon granules and Zeolytes 4A and 13X, then a slower passage through a (low-stream) tower filled with the

TABLE XVII
Plant Feed and “Field Grade” Hydrocarbon Analyses
(Typical month, at Dome Petroleum Ltd. Sarnia, Canada.)

Ingredients	Plant Feed	F.G. Propane	Per Cent By Weight	
			F.G. Isobutane	F.G. n-Butane
Methane	0.05	0.1	0.01	0.01
Ethane	1.7	2.9	0.03	0.02
Propane	50.3	94.9	2.4	0.4
Isobutane	9.8	2.0	96.2	1.9
n-Butane	17.3	0.1	1.3	96.0
Isopentane	5.0	0	0.05	1.9
n-Pentane	4.6	0	0.03	0.2
Hexanes, etc.	11.3	0	0	0
Unsaturated Hydrocarbons	0.03	0	0	0
Sulfur Compounds	trace	trace	trace	trace
Water	trace	trace	trace	trace

The in-plant feed is distilled to the “Field Grade” gases, plus condensate, consisting of about 18% of the in-feed and composed of C₃, C₆ and some C₇ hydrocarbons. For propane and n-butane, unsaturates are generally below 42 ppm. sulfur compounds are almost always below 0.6 ppm, according to one user.

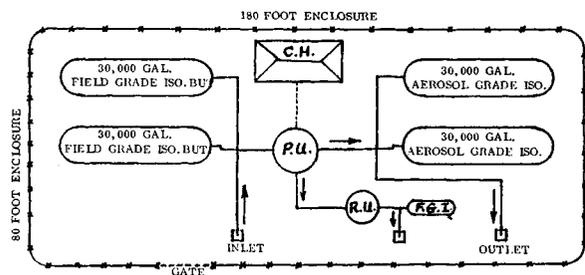


Figure 17. Butane Purification Facility

C.H. = Control House (14' x 28') P.U. = Purification Unit
 R.U. = Regeneration Unit F.G.I. = Fuel Grade Isobutane
 (Waste)

Cost: \$1,800,000 (1982)

Capacity: 3 million gallons per year

Available consultants: George A. Brock & Associates, Inc., and
 Linde Division, Union Carbide Corporation

same absorbents. Molecular sieve absorbents are supplied by W.R. Grace & Co. and the Linde Division. Each of the three absorbent materials has a well-defined spectrum of utility, and ratios should be selected in keeping with the type and amounts of impurities to be captured. For example, Zeolyte 4A is particularly useful as an absorbent for water.

For larger units (those above 1 or 2 million gallons of pass-through per year) it is generally recommended that absorbent reactivation equipment be installed. Eventually even a large tower will reach impurity saturation with respect to some specific ingredient. Then, if elution continues, some other impurity may be absorbed preferentially, displacing the saturated first ingredient as a line slug. For example, acetylene is weakly absorbed by the zeolytes, and once saturation occurs, it can be supplanted easily by such large-scale impurities as isobutylene. Pure acetylene has only a very slight odor, and without constant gas chromatographic surveillance, could easily be displaced totally into the Aerosol Grade propellant storage tank.

Depending upon the make-up of the field grade gas liquids and the size of the purification tower, anywhere from about 200,000 to 1,000,000 gallons can be passed through before impurities start to percolate into the finished product line and it becomes obvious that regeneration is necessary. Zeolytes in particular are expensive commodities, so that replacement is not feasible. They must be regenerated, either in site or at a remote service location.

There are two major types of regeneration equipment, both in the \$500,000 range: salt bath heaters and burning bed heaters. Both operate at about 700°F

(370°C). The salt bath heater of about 2.5 million BTU seems to be preferred. The tower is pumped free of any gas liquids and the absorbents are then heated for a four hour period, using hydrocarbon gas that has been heated by passage over a hot salt bath. After temperature is reached, the hot gas is pumped off to a cooling unit, carrying with it all the impurities, which may total as much as 2,000 to 4,000 pounds (907 to 1814 kg) depending on elutants and tower size. This takes about four hours and is followed by a final hour period for cool down of the unit.

A typical, well-conducted regeneration will only deplete absorptive efficiency by about 1 or 2%, due to powdering and unsaturated gas polymerizations on the zeolytes. However, if periods much longer than four hours are used for the two heat-utilizing stages, bed life can be shortened considerably.

At the cooling tower the heavily contaminated gas liquid will form a layer over the condensed water, allowing the water to be decanted and sewerred. The remaining 1,000 to 2,000 gallons (3,790 to 7,570 liters) of malodorous liquid gas can be eliminated in various ways, perhaps by being vended to a local fuel dealer as No. 5 Grade heating gas.

A typical 12,000 pound (5,440 kg) tower can hold up to about 110 pounds (50 kg) of acetylene, 1,050 pounds (476 kg) of unsaturates such as propylene, isobutylene, butadiene and so forth, and up to 3,000 pounds (1,360 kg) of any combination of water and sulfur compounds. Tower capacities are generally in the 8,000 to 16,000 pound (3,630 to 7,260 kg) range and nearly all installations have regenerative capacity built into the system.

At least two large marketer-fillers (captives) of aerosol products have purification towers to "polish" Aerosol Grade gas liquids for use in cosmetic products. Up to about 1979 some suppliers provided Aerosol Grade stocks relatively high in unsaturates, giving the products a rather stale, undesirable odor. As an example, the Aeropres Division used to offer two grades of propellant: Aerosol and Cosmetic grades. They were specified as having maximum unsaturate content of 1,000 ppm. and 100 ppm., respectively. But later on, manufacturing improvements allowed Aeropres to produce all their propellents with a maximum unsaturate content of only 10 ppm. This included the "Aeropres"® propellents (Aerosol Grade propane, n-butane and isobutane, plus propane/isobutane blends) and after June 1, 1980 the new "Aeropin"® blends made from propane and mixed butane feedstocks.

TABLE XIX

Typical Composition of Aerosol Grade Propellents

Composition (mol%)	Propane	Isobutane	n-Butane
Ethane	0.5 max.	—	—
Propane	95.0 min.	3.0 max.	1.0 max.
isoButane	5.0 max.	95.0 min.	3.0 max.
n-Butane	0.5 max.	5.0 max.	97.0 min.
Pentanes	—	0.1 max.	2.0 max.

lected. The beaker is swirled to facilitate evaporation. At the point where the last amount is about to volatilize the contents are sniffed for possible off-odor. In some cases odors are compared with those of standards. More propellent is rejected for off-odor than for any other reason, by far.

The gas/liquid chromatographic (GLC) analyses is aimed at determining the composition of the major components, those over 0.05 to 0.10%, rather than scanning for contaminants. A typical GLC trace is shown in Figure 18, for Aerosol Grade isobutane, using an instrument with integrator and recorder.

A recent CSMA publication contains a consensus of the hydrocarbon suppliers regarding the typical compositions for the three common propellents. They are shown in Table XIX.

To reduce this to a practical basis the figures may be compared with those listed on laboratory test reports covering tankcars of isobutane received from four major suppliers, as shown in Table XX. All four lots were approved as excellent, during 1980.

If a GLC assay yields good results, pressure testing may be superfluous, unless the partial pressure of air is in question. Unlike the CFCs, air is absent in hydrocarbon receipts, for all practical purposes. Pressure tests are normally made at 70°F (21.1°C), so that a direct comparison with the specification pressure range at that temperature can be made. For blends the 70°F (21.1°C) pressures should be that stipulated in the blend designation ± 2 psi (14 kPa).

Both suppliers and fillers often prefer to check pressures at temperatures between 60° to 80°F (15.6° to 26.7°C) instead of equilibrating the sample to 70°F (21.1°C). They then convert the result to 70°F (21.1°C) standard temperature by means of a chart. For example, an isobutane pressure of 36.00 psig at 75°F would convert to 31.75 psig at 70°F using a factor of 0.85 psig/°F. (In the ISO system, isobutane pressure

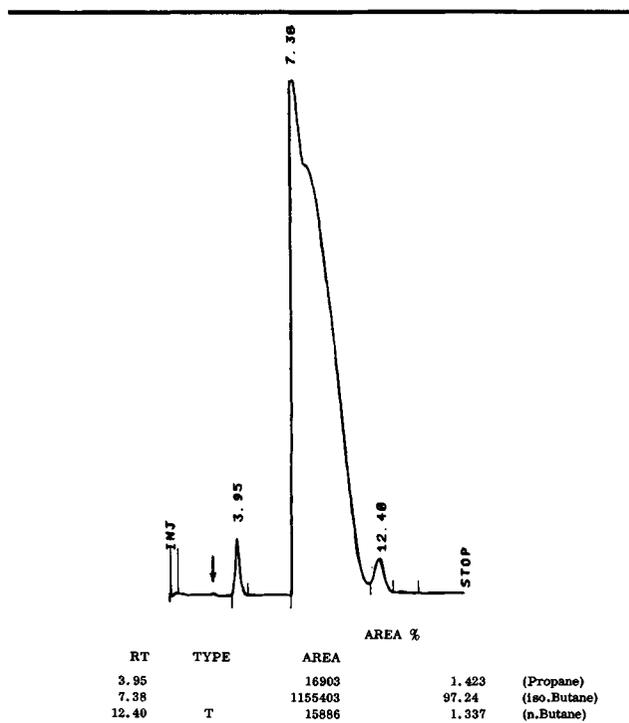


Figure 18. G/L Chromatographic Analysis of Aerosol Grade Isobutane

Supplier's analysis: 0.01% ethane, 1.91% propane, 96.08% isobutane and 2.00% n-butane (June 30, 1980).

Note: The arrow indicates a possible peak for ethane, not integrated in the illustrated analysis.

TABLE XX

Laboratory Results Accompanying Isobutane Shipments
(From four major Aerosol Grade suppliers)

Attribute	Company			
	A	B	C	D.*
C ₂ Ethane**	0.01			
C ₃ Propane	1.91	1.29	0.33	0.01
IC ₄ Isobutane	96.08	97.13	96.30	99.97
NC ₄ N-butane	2.00	1.58	3.37	0.02
C ₅ + (Isopentane, etc.)	0.00			
Unsaturation	< 0.0003			
Sulfur	0.0001			
Moisture	< 0.00012			
Residue (g/100 ml)	0.0001		Trace	
Acidity of Residue	Neutral			
Pressure (psig at 70°F)	31.95	31.5	30.9	31.0
Odor	Pass		Pass	Pass

*Supplier does not provide analyses. Tests performed by filler.

**GLC results supplied as mol. % and liquid volume %. Converted to mol. % throughout, for uniformity.

Note: All four lots approved by the filler as excellent quality.

In a survey of 100 lots of Aerosol Grade isobutane, the highest level of propane was 2.26% and the highest level of n-butane was 3.75%. The two lowest isobutane assays were 94.37% and 95.43%.

measured as 248.2 kPa at 23.9°C would change to a pressure of 218.5 kPa at 21.1°C, using a conversion factor of 10.6 kPa/°C.)

A similar technique is used for measuring the specific gravity of bulk shipments. Prices are based upon U.S. Gallons at 60°F (15.6°C). For example, a standard tanktruck with a water capacity of 10,450 gallons is 79v% loaded with 8,255 gallons of isobutane at a temperature of 75°F (23.9°C). Using a temperature conversion factor of 0.981 the volume is changed to 8,098 gallons at 60°F (15.6°C). If the truck is weighed before and after unloading payment is made according to weight loss, converted to U.S. Gallons at 60°F (15.6°C) by dividing the weight loss in pounds by 4.6937 pounds of isobutane per gallon at that temperature.

Chemical tests are rarely performed during inspections of hydrocarbon propellents. If a chlorine or hypochlorite bleach type odor is detected, it may be due to tertiary butyl hydroperoxide (CH₃)₃C.O.OH, produced in situ by Grignard RMgCl or other types of reactions. A sophisticated laboratory can detect this

contaminant by GLC procedures, but wet-method testing for peroxide moieties is often sufficient in assigning cause. If acetylene is suspected for any reason, the same philosophy applies. It can be determined by GLC instrumentation, but also by the simpler procedure of bubbling the gas liquid through ammoniacal copper (I) or silver (I) solutions to precipitate the sparingly soluble metallic acetylides. (Caution! These are explosive when dry and should be destroyed with acid.)

Properties of the Aerosol Grade Hydrocarbons

Over half of the total consumption of aerosol hydrocarbons is in the form of the individual gas liquids. For example, nearly all antiperspirants and many hair sprays use isobutane. On the other hand, n-butane is almost never used any more as a single propellant, due to the sensitivity of such products to variations in temperature. At one time the two largest volume window cleaners were pressurized with n-butane, since somewhat less was needed than with isobutane. But at temperatures below about 55°F (12.8°C) the air-free

TABLE XXI
Physical Properties of Purified Hydrocarbon Propellents

Property	Ethane*	Propane	Isobutane	N-butane	Isopentane*
Formula	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₄ H ₁₀	C ₅ H ₁₂
Molecular Weight	30.06	44.09	58.12	58.12	72.15
Vapor Pressure (psig at 70°F)	543	109.3	31.1	16.92	-3.5
Freezing Point (°F) (1 atm.)	-297.8	-305.9	-255.3	-216.9	-255.8
Boiling Point (°F) (1 atm.)	-127.5	-43.7	10.9	31.1	82.2
Specific Gravity (liquid) (60°F)	0.35	0.508	0.563	0.584	0.620
Specific Gravity (gas) (60°F) (Air = 1)	1.02	1.55	2.01	2.08	2.61
Critical Temperature (°F)	90.1	206.2	274.8	305.6	370.0
Critical Pressure (psig)	707.1	616.1	528.1	550.1	482.6
Critical Density (g/ml)	0.203	0.220	0.221	0.228	0.234
Flash Point (°F)	< -200	-156	-117	-101	< -60
Lower Explosive Limit (v% in air)	3.12	2.20	1.78	1.84	1.39
Upper Explosive Limit (v% in air)	15.0	9.51	8.40	8.48	7.97
Heat of Combustion (BTU/lb.)	22,190	21,620	21,298	21,318	21,102
Dispersion (Gas at 1 atm and 70°F)					
From 1 g (ml)	793	540.2	414.0	400.6	na
From 1 ml (ml)	276 est.	272.3	229.3	233.9	na
Solubility of Water in Propellant (70°F)	0.031	0.0168	0.0088	0.0075	0.0063
Solubility of Propellant in Water (70°F) (w% at 1 atm)	0.008	0.0079	0.0080	0.0080	0.0084

*Usually considered as co-propellents — present in commercial propellents.