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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.

pressure sank below 9 psig (62 kPa) and the spray deteriorated to one with a streaming center.

The physical properties of the purified hydrocarbon propellents are given in Table XXI.

The only ones of real importance to the formulator are the pressures, densities and flammability. As a consequence, supplementary information on pressures is provided in Figure 19., and data on the variation of density with temperature is shown in Figure 20. The degree of flammability can be measured in terms of BTU/lb. (as one of several criteria). The BTU values of the hydrocarbons are very high, and they are compared with those of the lower alcohols and other important aerosol ingredients in Table XXII.

Ethane is a relatively high pressure gas, now used only because it is a co-propellant almost always found in propane. It has no odor and is completely inert physiologically. It is available in states of high purity, since the only practical contaminants, methane and ethylene, are considerably more volatile. It may be purchased in five-foot cylinders, but the propellant suppliers continue to state that they have no plans to sell ethane in larger vessels. One intriguing idea has been to "beef up" Aerosol Grade propane by the addition of up to about 7.6w% ethane. This would act to elevate the pressure to 156.0 psig at 70°F (1.076 MPa at 21.1°C) which is the same as Polymerization Grade propylene.

Thus, such a blend could be transported in tankcars like propylene, but higher pressure compositions could not. Theoretically, such a blend should be about 3.5% less costly than propane. It should also possess about 16 to 20% more dispersive power, depending upon the properties of the aerosol concentrate.

Ethane has been used in the formulation of a number of experimental aerosol products, often with satisfactory results, but these have come to nothing because of both the supply problem and the fact that it could usually be replaced with either carbon dioxide or nitrous oxide, which have pressures about 44% higher than ethane and solubilities about 25 to 30% lower. Ethane would have to be introduced into aerosol units using instantaneous impact gassing techniques on either T-t-V or U-t-C gassing equipment, unless an explosion-proof gasser-shaker was available in a suitable enclosure.

Propane is a fairly high pressure propellant and is used either pure or in blends whenever a propellant pressure of greater than 31 psig at 70°F (214 kPa at 21.1°C) is needed. Outside the U.S.A. it is sometimes used at concentrations of about 8 to 9%, with a preponderance of P-11 and concentrate levels of 10 to 20%, in order to give non-flammable sprays of excellent break-up. At least 30 to 35% P-12 would be required for the same dispersibility. Propane is also

TABLE XXII

Heat of Combustion for Various Aerosol Ingredients

Ingredient	Molecular Weight	BTU/lb.	Kg-cal.		
			100 g	BTU/gMW	
				Kg-cal. gMW	
Ethane	30.05	22,190	1226	1463	368.4
Propane	44.06	21,620	1195	22089	526.3
iso-Butane	58.08	21,298	1183	2728	687.2
Pentane	72.15	21,152	1163	3328	838.3
Hexane	86.21	20,887	1150	3930	989.9
Heptane	100.22	20,741	1144	4552	1146.5
Octane	114.24	20,601	1140	5171	1302.7
Nonane	128.26	20,471	1137	5789	1458.3
Decane*	142.29	20,376	1132	6392	1610.2
Undecane**	156.31	20,304	1128	6999	1763.1
Methanol	32.03	10,238	533.5	679	170.9
Ethanol	46.05	13,309	711.4	1300	327.6
isoPropanol	60.10	14,390	799.5	1908	480.5
Dimethyl Ether	46.05	13,586	754.8	1380	347.6
Acetone	58.08	13,226	734.8	1694	426.8
Methylene Chloride	84.93	2,262	125.7	424	106.8

Heats relate to combustions initiated at 20°C and one atmosphere, resulting in gaseous CO₂, liquid H₂O and heat. Hydrocarbons through pentane, as well as dimethyl ether, are burned in the gas state.

*Corresponds to mineral spirits or light kerosenes.

**Corresponds to standard kerosenes.

used in conjunction with combinations of about one-part methylene chloride and three-parts 1,1,1-trichloroethane (and up to 10% active materials) to produce heavy, residual sprays (at about 10%) or typical space sprays (at about 16%). A number of automotive products use propane as the propellant, because it is able to disperse heavy oils, greases, undercoatings and similar concentrates when used at 12 to 20% levels.

Propane, along with the butanes and pentanes, is characterized by non-polarity, a total lack of hydrogen bonding, and very poor solubility in conjunction with polar substances, such as water, glycols, certain hair spray fixatives and many perfume ingredients. One measure of solvency is Kauri-Butanol value: a measure of incompatibility with a solution of Kauri resin in n-butyl alcohol. This is an old test and the results are somewhat artificial, but still used widely. A more fundamental measure of solvency is the solubility parameter concept, developed in 1916. It is a measure of Keesom (hydrogen bonding) forces and other forms of molecular attraction. When substances have similar solubility parameter values, they are usually miscible. Where a solution has a solubility parameter value close to that of an aerosol sealing gasket, there will most likely

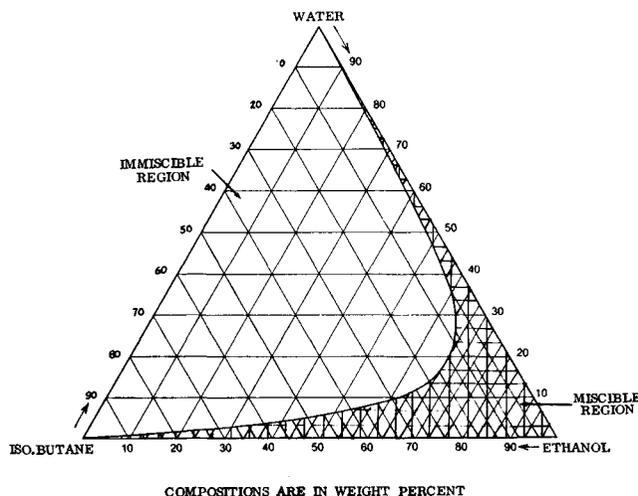


Figure 21. Solubility of the Ethanol, Water and Isobutane System at 70°F (21.1°C)

be severe valve leakage and elastomer swelling, regardless of hydrogen bonding capacities. The K-B and S-P values for propane and other hydrocarbons are included in Table XXIII.

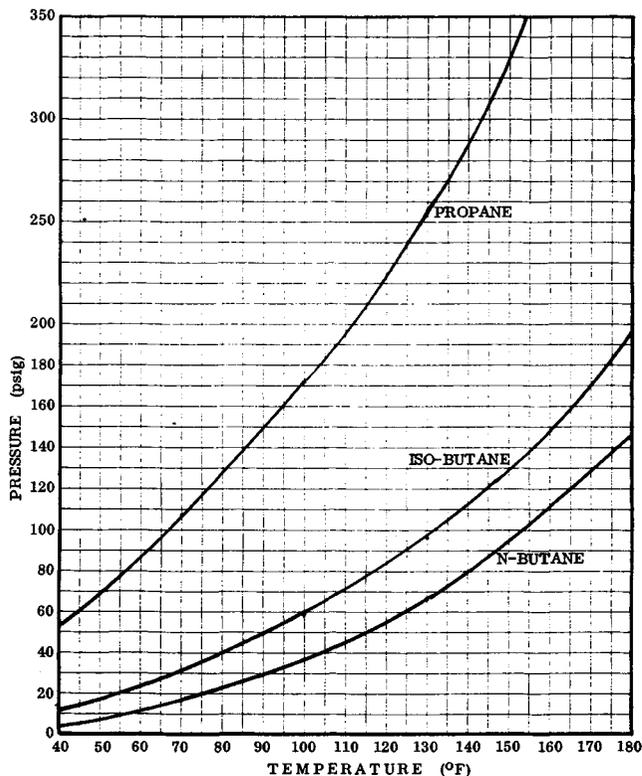


Figure 19. Pressure of Hydrocarbon Propellents at Various Temperatures

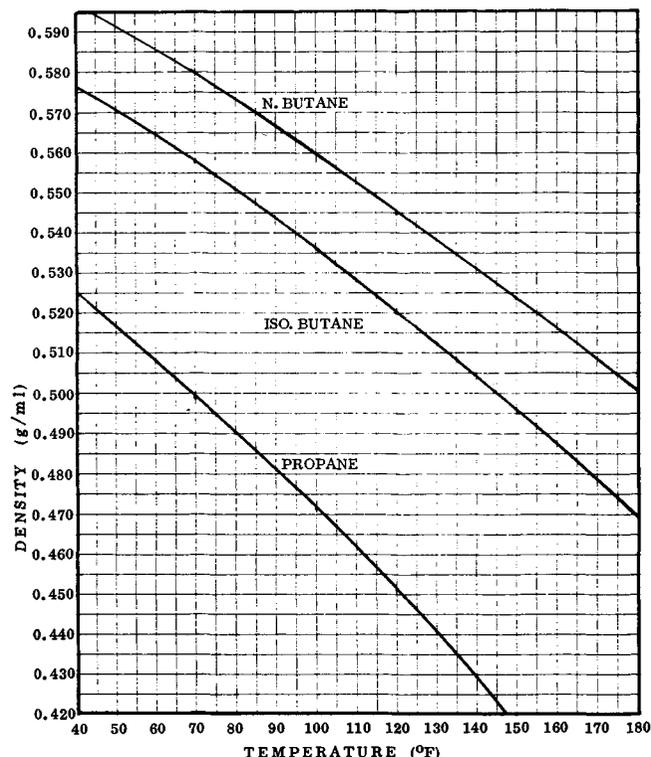


Figure 20. Density of Hydrocarbon Propellents at Various Temperatures

Propane and the butanes are essentially insoluble in water. However, modest percentages of water can be included in such products as disinfectant/deodorants and hair sprays by taking advantage of the co-solvent effect of ethanol. For example, if 69.5% ethanol is present in a formulation, the remaining 30.5% of water and propane can consist of any ratio of these two components and remain as a one-phase solution at 70°F. For isobutane/ethanol/water systems, those with over 68.0% ethanol are miscible and in the case of n-butane/ethanol/water compositions, ones with over 68.8% ethanol are always soluble. This relationship is illustrated in the case of isobutane/ethanol/water by means of a triangular graph, Figure 21.

Isobutane is the workhorse of the hydrocarbon propellents, often used in a non-blended form, since the pressure of about 31 psig at 70°F (214 kPa at 21.1°C) is sufficient for many applications. Although the distinction is more or less academic, isobutane (and n-butane) may be considered slightly more flammable than propane. They have lower LELs, and the vapors are heavier and tend to collect in floor level areas more readily. Comparing the combustion equations:

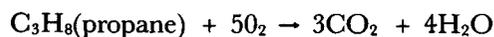


TABLE XXIII

Solvent Properties of Propellents and Other Substances

Substance	General Solvency	Hydrogen Bonding	Kauri-Butanol Value	Solubility Parameter
Propane	Poor	0	15.2	7.1
Isobutane	Poor	0	17.5	7.1
n-Butane	Poor	0	19.5	7.1
Isopentane	Poor	0	21.3	7.1
Mineral Spirits	Poor	0	34 - 40	7.2
P-11	Good	0	60	7.5
P-12	Poor	0	18	6.1
P-22	Fair	Fair	25	6.5
P-113	Fair	0	31	7.2
P-114	Poor	0	12	6.2
P-142b	Good	Low	20	6.8
P-152a	Good	Low	11	7.0
P-C318	Very Poor	0	10	5.0
Dimethyl Ether	Very Good	High	91	7.3
Methylene Chloride	Excellent	Good	136	9.5
Chloroform	Excellent	Good	208	9.1
Carbon Tetrachloride	Excellent	0	113	8.6
Ethanol	Very Good	High		12.8
Isopropanol	Very Good	High		11.9
n-Butanol	Good	Fair		11.4
MEK	Very Good	High		9.3
MIBK	Very Good	High		8.4
Butyl Acetate	Very Good	High		8.4
Butyl Cellosolve	Very Good	High		8.9
Toluene	Very Good		105	
Xylenes	Very Good		95	
Buna N	na	—*	na	9.4
Neoprene GN	na	—**	na	9.2
Butyl Rubber	na	—**	na	8.1
Natural Rubber	na	—*	na	8.3
Polyethylenes	na	—**	na	7.4

Notes: Substances having similar solubility parameters will usually be miscible.

Where solutions have solubility parameters near those of valve elastomers pronounced swelling and valve leakage may result, regardless of hydrogen bonding capabilities.

*High hydrogen-bonding capacity.

**Low hydrogen-bonding capacity.

***Zero hydrogen-bonding capacity, except for certain parameters.

The isothermal increases in gas volume are 17% and 20%, respectively. In a closed space, this would give only a slight increase in pressure. The large pressure increase noted during fires or explosions is due mainly to the temperature effect. At the LEL, for instance, 1.8v% of isobutane will combine with 11.5v% of oxygen in a chemical reaction generating intense heat. This heat instantly dissipates through the 86.7v% of non-reacting molecules (mainly nitrogen) in the mixture and causes an immediate expansion to several times the original gas volume in accordance with Charles' Law. If there is an impediment to this expansion, then the pressure will increase and the impediment (such as a room or building) may or may not give way.

When the isobutane concentration increases beyond 3.0% it is then capable of reacting with all the oxygen in the gas mixture and must then reach beyond the immediate reaction locale to find additional oxygen. Reactions at supra-LEL levels are substantially more violent than those at the LEL, with both flame travel rate and fireball size being magnified. When the pressure increase gets to more than 0.04 psi (0.28 kPa) windows may blow out, roofs may bulge and other things may happen in the resulting "whoosh". At less than this level the pressure increase may be felt only in the ears. The key to all this is the relationship of the amount of flammable gas mixture to the size of the enclosure, and, to some extent, the sturdiness of the construction.

Isobutane is the most common propellant for anti-spirants, window cleaners, starches, hair sprays and a host of other aerosol products. Many aerosol fillers use it also in the production of lighter fluids and refill tubes. For paints, shaving creams and other applications where higher pressure propellents are needed, isobutane is commonly blended with propane, by either the supplier or the filler, using explosion-proof proportioning blending equipment.

n-Butane is rarely used in the pure form, but it does find a minor place in the production of some colognes and perfumes, being used at about 16% to 20% of such formulations. Its low pressure of 17 psig at 70°F (117 kPa at 21.1°C) makes the spray pattern susceptible to deterioration at temperatures below 55° to 60°F (13 to 16°C). Nearly all the n-butane that finds its way into aerosols does so in the form of blends: up to about 4% in compositions high in isobutane, and up to 60% in blends of propane with the unseparated butanes, as is discussed later.

Isopentane is the last hydrocarbon propellant of any significance. Since it has a boiling point of 82.2°F (27.9°C) it is a very volatile liquid and not a true propellant. It occurs as a co-propellant in certain commercial and Aerosol Grade blends, particularly those of propane and the natural butane mixtures, where it may get as high as 3.0%. In the pure form it is used as a latent puffing or foaming agent in certain Sepro-can type shaving creams.

There are two major roadblocks that must be overcome before isopentane can be a higher volume aerosol ingredient: odor, and its unique flammability hazards. The highly purified material can be purchased in tankcar or (at least formerly) tanktruck quantities, but not as an Aerosol Grade material. One supplier will (somewhat reluctantly) spot-check the odor level of available tankcars and ship the lowest ones to interested aerosol customers, who may or may not have their own purification towers. The odor level of hand-picked, good quality lots of Commercial Grade (gasoline grade) isopentane is generally very close or even equal to that of the purified material. The odor of the hydrocarbon itself is slightly higher than that of isobutane, but comparable with that of n-butane. Except under rather unusual circumstances the odor of isopentane is not a formulating problem.

Because isopentane is such a volatile and flammable liquid it has been treated as a true propellant in filling plants. Using sealed systems, the material is pressure loaded into containers using T-t-V or U-t-C techniques. But, even here it is felt that isopentane may pose an extra or even unacceptable level of hazard, due to the fact that it is essentially a liquid substance. For instance, a rupture of a 600 to 800 psig (4.14 to 5.52 mPa) isopentane hose in the gas house could act to release a rather large amount of liquid before a sufficient quantity of gas is produced, so that the detection system would sense it and react by electrically activating the interlock circuitry. If a fire was initiated the fuel pool on the floor could sustain it, in spite of some of the sprinkling systems now in use. Such a situation would not occur with propane or the butanes, since they would not form liquid pools unless very cold (and non-warmed) propellant supplies were being used.

Isopentane has been used in at least a million cans of hair spray, with typical formulations consisting of about 5.5% CO₂, 15% isopentane, 12% methylene chloride and 67.5% ethanolic concentrate. They provided extraordinarily good spray patterns at all stages of use,

but were discontinued in favor of formulas that were safer for the plants to produce.

The "fuel pool" disadvantage of isopentane is eliminated if the material is brought into the gas house as a blend with propane. Since isopentane is only slightly higher in price than propane, such blends are economically attractive. Some filling has been done with such blends. The so-called distillation effect, where propane would preferentially escape from the liquid phase, is not a problem, provided the propane content of the total formulation is over 10 to 12% and a non vapor-tap valve is used. Certain higher pressure propane/isopentane blends can be used with vapor-tap systems. In any case, since the propellant suppliers do not blend isopentane with Aerosol Grade propellents, such mixtures have to be produced by the fillers themselves.

Blends of Hydrocarbon Propellents

Almost half of the hydrocarbon aerosol market is held by blended gas liquids. The oldest and still the most common mixtures are combinations of propane and isobutane, giving pressures which range from 31 to 109 psig at 70°F (214 to 752 kPa at 21.1°C). The lower pressure blends of this series are the most popular.

The propane isobutane mixtures are most commonly identified in the U.S.A. by designations such as A-36, A-40, C-70, C-85 and so forth. The "A" stands for Aerosol Grade and the "C" stands for Commercial Grade. The number which follows signifies the pressure at 70°F (21.1°C), with a pressure specification generally ± 2 psi (14 kPa) from that figure.

The various "A" type designations, such as A-36, were copyrighted with the U.S. Patent Office by Phillips Petroleum Co. during the 1950's, when they pioneered the Aerosol Grade products and blends. The terms became very popular and are used generically by almost everyone in the aerosol industry. That liberty is taken here, for simplicity, but recognizing that they are Phillips Petroleum Co. trademarks and that the industry owes this company much for their foresighted investment into specially purified aerosol propellents that are so important to us today.

Outside of the U.S.A. and Canada, these blends are identified by stating the ingredients and the pressure in bars at 20°C (68°F); for example: propane/isobutane, 2.7 bars. This mixture is the equivalent of A-41.7 in the Phillips Petroleum Co. designation, assuming the hydrocarbons are in a purified state.

Propane/isobutane blends are also identified in terms of mol%, volume% and weight% by the suppliers, and this has led to a great deal of confusion in the filling segment of the industry. Since weight is the basis on which virtually all aerosols are formulated and filled, various supplier data expressed in mol% and volume% must be laboriously converted to weight% in order to be meaningful. Charts and graphs are available to help make the conversion, and a short summary of the inter-relationship is provided here as Table XXIV.

The table is idealized, as if only mixtures of ultra-pure propane and isobutane were involved, when actually up to 5% of other hydrocarbons can be present within the scope of the Aerosol Grade specification. Thus, a typical composition for A-46 might be 0.08% ethane, 19.59% propane, 78.34% isobutane, 1.97% n-butane and traces of other components.

The pressure of several standard blends is given at various temperatures in Figure 22 and the density versus temperature relationships of the same mixtures are shown in Figure 23 (Page 350).

Blends have been made commercially using isobutane and n-butane. Of these, only A-24 is significant, but others include A-20, A-28 and A-29. They are of some interest in the formulation of glass aerosol products.

TABLE XXIV

*Conversions Between Mol, Volume and Weight
Per Cent for Blends of Propane & Isobutane*

Pressure (psig 70°F)	Pressure (kPa 21°C)	Propane Content		
		Mol%	Volume %	Weight%
31.1*	214	0	0	0
34.0	234	3.8	3.2	2.9
40.0	276	11.4	9.8	8.9
46.0	317	19.0	16.5	15.1
52.0	359	26.8	23.5	21.7
59.0	407	35.6	31.7	29.6
62.0	427	39.5	35.5	33.1
67.0	462	45.9	41.7	39.2
70.0	483	49.8	45.5	41.9
76.0	524	57.3	53.1	50.6
80.0	552	62.5	58.4	55.8
85.0	586	68.9	65.1	62.7
92.0	634	77.9	74.8	72.8
96.0	662	83.0	80.4	78.7
109.1**	754	100.0	100.0	100.0

*Aerosol Grade isobutane; known as A-31.

**Aerosol Grade propane; known as A-108.

All other compositions are standard industry blends now in commercial use, e.g. A-34, A-40, A-46, etc.

About 1979 the n-butane/propane series of propellant blends became commercially important. They had always been available, but in 1979 they were starting to be priced lower than comparable pressure isobutane/propane mixtures. This was a reflection of the considerably lower price tag for field grade n-butane, compared with field grade isobutane. It was inappropriate to call these blends by the A-17 to A-108 type designations, since this would invite confusion with the standard isobutane/propane compositions. As a result, a series of other terms were developed. For example, the 46 psig at 70°F (317 kPa at 21°C) blend became known as Aeropres B-46, Aeron NP-46 (Diversified), Propellant BP-46 (Phillips), and so forth.

At least nine of these n-butane/propane blends have been sold commercially. A listing of stylized compositions (as if they contained only ultra-pure n-butane and propane) is provided in Table XXV, along with pressure and density figures for 70°F and 130°F (21.1°C and 54.4°C).

An examination of these mixtures as possible replacements for isobutane or isobutane/propane blends shows that they do not have quite as much dispersant ability. This minor shortcoming can be corrected by using about 1.08 times as much propellant in

the formula, or by revising the composition to the next higher pressure level. (Intermediate blends can be supplied as easily as the standard ones, if needed.) The higher pressure approach is generally the easiest for the formulator. Any slight increases in delivery rate can be removed by selecting a valve with a slightly smaller rate-limiting orifice size. As the amount of propane in the n-butane/propane blends increases, there is less and less need for such adjustments, since the n-butane, which causes the differences, is diluted into relative insignificance.

During the spray-down of any aerosol composition, except an air-free ultra-pure single propellant, the pressure moves downward, rather fast at first as head space air is diluted, and then more slowly, due mainly to evaporation of propellant out of the liquid phase into the expanding head space. If the propellant consists of a blend, the pressure decreases during use at a rate somewhat greater than is the case for a single propellant. Where the formulation contains a relatively high percentage of propellant, the distillation effect is reduced, since the liquid composition is changed less by evaporation of the most volatile components into the enlarging head space.

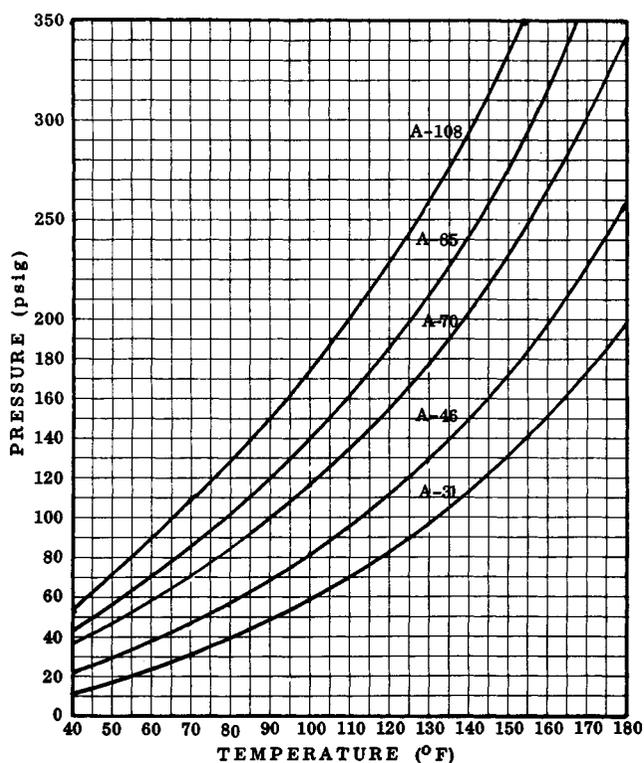


Figure 22. Pressure of Propane/Isobutane Propellents at Various Temperatures

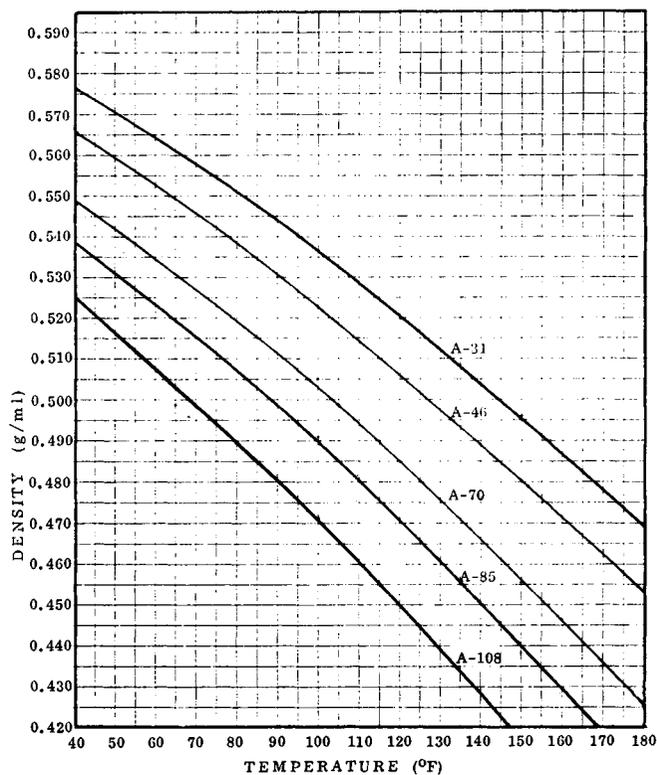


Figure 23. Density of Propane/Isobutane Propellents at Various Temperatures

This is illustrated by taking a standard anhydrous hair spray as an example, where the commercial formulation consists of a concentrate, plus 20% A-31. By substituting a blend of n-butane/propane (31 psig 70°F for 214 kPa at 21°C) for the isobutane, the pressure will decrease during use as shown in Table XXVI.

The delivery rate drops significantly and the quality of the spray deteriorates during the second half of the can spray out. By using a higher pressure blend of n-butane/propane the quality of the spray pattern is improved, but changes in delivery rate. Relative fineness of the particles still change as a result of the selective evaporation of the rather small propane inventory.

The n-butane/propane blends in the range of B-70 to B-90 work much more satisfactorily, and are virtually indistinguishable from the regular A-70 to A-90 blends. They are used to a significant extent in paint and coatings, and in several automotive products.

The use of vapor-tap valves places an additional strain on the n-butane/propane blends, since propane is

lost not only to the expanding headspace, but to the atmosphere as well, through the valve vapor-tap orifice. Such valves should be used with n-butane/propane blends only when the relative amount of propane is reasonably high, and when the percentage of propellant blend is rather high as well.

Before leaving these blends, a small economic aspect should be noted. Considering A-31 and B-31 as an example, the density of A-31 is 0.564 at 60°/60°F (15.6°/15.6°C), while that of B-31 is 0.5736 at the same references. The difference in density is 1.7%. Since hydrocarbons are purchased by the gallon and sold by the pound, there is an additional economic incentive of 1.7% (roughly \$0.02/gallon) to purchase B-31 instead of A-31. However, as greater amounts of propane are included in the "B-" blends, the incentive becomes less.

In June, 1980, after about two years of research and preparation, Aeropres Corp. introduced their Aeropin blends. They are prepared from combinations of propane with naturally occurring n-butane/isobutane

TABLE XXV

Composition and Physical Properties of n-Butane/Propane Propellant Blends

Propellant Blend	Propane Level		Pressure (psig)		Density (g/ml)	
	Mol%	Wt. %	70°F	130°F	70°F	130°F
B-24*	8.0	6.2	24	81.4	0.570	0.530
B-31	16.0	12.6	31	96.1	0.565	0.523
B-40	25.0	20.2	40	114.4	0.558	0.513
B-46	31.7	26.1	46	126.4	0.553	0.506
B-59	44.7	38.0	59	153.0	0.543	0.494
B-70	57.5	50.7	70	176.3	0.535	0.485
B-80	68.3	62.1	80	198.0	0.527	0.474
B-85	73.7	68.0	85	207.2	0.522	0.467
B-90	79.0	74.1	90	219.0	0.517	0.459

*Aeropres B-24, Aeron NP-24 (Diversified), Propellant BP-24 (Phillips), or like blend from other propellant suppliers. The same for other propellant designations.

TABLE XXVI

Decrease in Pressure as Aerosol Hair Spray is Discharged

(For hair spray, with 20.0% propellant.)

Propellant	Pressure (psig at 70°F or 6.89 kPa at 21°C) Per Cent of Product Dispensed				
	0	25	50	75	99
A-31	30	23	22	20	17.5
B-31*	30	19	16	14	12.5
BI-31**	30	20	17	16	14.5
BI-34	33	22	20	18	16.0
BI-36	35	23.5	22	20	17.0

*Aeropres B-31, Aeron NP-31 (Diversified), Propellant BP-31 (Phillips), etc.

**Aeropin 31 (Aeropres), Aeron NIP-31 (Diversified), Propellant IBP-31 (Phillips), etc. Approximately 8w% propane, 37w% isobutane and 55w% n-butane.

stocks. These stocks may contain up to about 3 mol% isopentane, so this co-propellant must be considered also. The economic attraction is that the distillation step used normally to separate the isomeric butanes need not be conducted. The Aeropin butanes are drawn from east Texas gas wells where the concentration of isobutane is unusually high, approximately 40.0 w% of the total butanes content. The Aeropin propellents start

with Aeropin-24 and then, by adding increasing amounts of propane, they extend upward to Aeropin-70. By 1981 other hydrocarbon suppliers also offered equivalent series of propellant blends. The Phillips products were called Propellents A-(number) IBP and the Diversified blends were designated Aeron NIP-(number), for example. A comparison of the compositions of A-46, B-46 and BI-46 propellents is provided in Table XXVII.

TABLE XXVII

Typical Compositions for Hydrocarbon Propellant Blends Having a Gauge Pressure of 46 psig (3.22 kg/cm² or 317.1 kPa) At 21.1°C (70°F)

Ingredients	Per Cent by Weight		
	Propellant A-46* Aeropres 46** Aeron A-46***	Propellant A-46*BP Aeropres B46** Aeron NP-46***	Propellant A-46*IBP Aeropin 46** Aeron NIP-46***
Ethane	0.08	0.25	0.29
Propane	19.59	26.00	21.67
Isobutane	78.34	2.00	30.09
n-Butane	1.975	69.236	45.236
Pentanes	0.010	2.500	2.700
Hexanes	0.001	0.010	0.010
Unsaturated Hydrocarbons	0.001 (max.)	0.001 (max.)	0.001 (max.)
Sulfur Compounds	0.0005 (max.)	0.0005 (max.)	0.0005 (max.)
Water	0.0025 (max.)	0.0025 (max.)	0.0025 (max.)

*Trademark of the Phillips Petroleum Company.

**Trademarks of the Aeropres Corporation.

***Trademark of the Diversified Chemicals and Propellents Co.

TABLE XXVIII

Typical Compositions of the Aeropin Propellents
(Considering only propane, isobutane and n-butane)

Propellant	Density (60°F)	Composition	Propane - Isobutane - N. Butane (Weight Percent)	Typical
Aeropin-24*	0.5742	1.65	39.29	58.96
Aeropin-29	0.5708	6.19	37.53	56.28
Aeropin-31	0.5696	8.03	36.78	55.19
Aeropin-46	0.5591	22.27	31.09	46.64
Aeropin-52	0.5547	28.34	28.67	42.99
Aeropin-70	0.5411	47.93	20.83	31.24

*Registered trademark of the Aeropres Corp.

Typical Compositions of the Phillips BIP Propellents

Propellant	Ethane	Composition (Weight Per Cent) Typical**			
		Propane	Isobutane	n-Butane	Pentanes
A-31* BIP	0.0	9.0	36.1	54.2	0.7
A-46* BIP	0.0	22.2	30.9	46.4	0.5
A-70* BIP	0.0	47.7	20.7	31.3	0.3
A-80* BIP	0.0	60.6	15.7	23.5	0.2
A-85* BIP	0.0	66.9	13.1	16.8	0.2

*Registered trademarks of the Phillips Petroleum Co.

**Specification maximums for ethane = 1 mol%, and for pentanes = 1.5 mol%.

The BI- propellents (propane, isobutane/n-butane blends) are true Aerosol Grade products. The saturates content is above 99.99 mol%, and unsaturates are below 0.001%. Moisture is below 25 ppm and typically 1 ppm. Sulfur is below 5 ppm and typically below 1 ppm. Residue, acidity of residue, odor and so forth are comparable to the Aerosol Grade propane and isobutane blends. Typical compositions of these new propellents are shown in Table XXVIII for two major suppliers. Compositions offered by other suppliers are equivalent.

The pressure drop during use is greater than for the propane/isobutane blends, but less than for the propane/n-butane mixtures, as would be anticipated. Small orifice vapor-tap valves can be used for certain

products, provided the percentage of propellant is rather high. It helps to have a higher pressure blend for these applications, to provide a greater inventory of propane for its preferential volatilization from the concentrate, which occurs during use. A marginal situation is encountered in the case of antiperspirant formulas, which commonly contain about 68 to 74% propellant, but where lower pressure types are used, principally isobutane or sometimes A-40. The data presented in Table XXIX represents results obtained in a study conducted on a commercial antiperspirant.

To complete the discussion of hydrocarbon blends, the combination of propane and isopentane is mentioned, again with the caution that it is theoretically very inexpensive, yet not readily obtainable on a commercial basis. In this case, because of the wide

TABLE XXIX

Effect of Propellant Selection on the Properties of a Typical Antiperspirant

Propellant	Initial Delivery Rate (g/s.)	Initial Flame Prog'n. (in.)	Initial Spray Pattern Diameter (" at 7")	Delivery Total (g.)	Residual Weight (g.)	Initial Solids Transfer Efficiency	100%	Pressure - psig, 70°F (21.1°C)			25%
								Fill Amounts			
								75%	50%		
A-31*	0.61	19	1.5	114.9	2.3	48.8%	34	32	31	30	
A-31**	0.60	19	1.5	115.0	2.1	48.0%	33	30	29	27	
Aeropin-31	0.61	19	1.5	116.5	1.3	48.7%	36	30	28	27	
Aeropin-34	0.63	20	1.7	117.1	1.5	49.6%	38	33	31	29	
Aeropin-36	0.64	21	1.8	116.3	1.7	48.0%	40	35	32	29	
Aeropin-40	0.66	22	1.7	116.8	1.5	47.2%	45	38	37	34	
Aeropin-46	0.69	24	1.9	116.2	0.9	43.1%	51	45	41	38	

*Production control units - vacuum crimped at 200"Hg°.

**Laboratory control units - vacuum crimped at 20" Hg°.

- Notes:
- All results represent the average of six cans tested.
 - The spray pattern of units pressurized with Aeropres 34 and 36 most closely matched the particle size and pattern of the standards, throughout the life of the test cans.
 - While Aeropin blends were selected in this test series, other propane/isobutane/n-butane blends of essentially the same composition should give fully equivalent results.

TABLE XXX

Composition and Pressures of Various PIP Propellents
(Propane and isoPentane)

Propellant	IsoPentane Content (wt %)	Pressure (psig)			
		70°F	100°F	130°F	160°F
PIP-(-3)	100	-3	6	20.5	40
PIP-17	89	17	32	53	—
PIP-31	80	31	50	78	—
PIP-36	76	36	59.5	90	126
PIP-40	73	40	65	97	135
PIP-46	68	46	74	109.5	149.5
PIP-60	56	60	95.5	138	179
PIP-70	47	70	111	158	—
PIP-80	38	80	127	180.5	—

Note: These blends were not commercially available in 1982; however, interested fillers might be able to mix their own requirements.

discrepancy in vapor pressure between the two component hydrocarbons, distillation effects can be expected to be at a maximum. The most useful of these blends are the higher pressure ones, used preferably at reasonably high concentrations in the total product. Table XXX provides composition and pressure data on these so-called PIP compositions.

In a second study, this time involving an anhydrous insecticide high in 1,1,1-trichloroethane and carrying 30% of hydrocarbon propellant blend, particle size measurements were taken at the 100% full, 50% full and 25% full levels, to compare the break-up of the A-70 standard propellant with both a propane/isobutane/n-butane (PIN-70) blend and the propane/isopentane (PIP-70) blend as the dispensers were emptied isothermally at about 70°F (21.1°C). The results of this Malvern type analysis are shown in Table XXXI and also in a particle size profile in the Aerosol Toxicology chapter, Figure 8.

The data show that both the A-70 and PIN-70 propellents give comparable results, whereas the PIP-70 particulation is a bit coarser, but probably acceptable commercially, and undoubtedly correctable by changing to a higher pressure blend, such as PIP-80.

Ether Type Aerosol Propellents

These propellents are not yet commercially significant in the U.S.A. or other countries in the Western Hemisphere, but one (dimethyl ether, or DME) has achieved fairly large scale use in certain European countries and in Japan. DME is said to account for 20% of the aerosol unit production in Belgium (1980), 17% of that in The Netherlands (1980) and 18% of the total in Japan (1979). About 22 million pounds (10,000 metric tons) were produced in Europe in 1980, account-

Propellant	Can	Fill	Mean Diameter (μm)
A-70	1, 2 & 3	100%	25.63
A-70	1, 2 & 3	50%	29.25
A-70	1, 2 & 3	25%	36.25
Aeropin-70	4, 5 & 6	100%	22.18
Aeropin-70	4, 5 & 6	50%	30.88
Aeropin-70	4 & 5	25%	30.62*
PIP-70	7	100%	20.03
PIP-70	7	50%	33.72
PIP-70	7	25%	41.07

*Can 6 (25%) input deleted from average — appears to have developed vapor-tap characteristics.

TABLE XXXI

Particle Size Distribution of an Anhydrous Insecticide Spray (Malvern Analyser) (36% Hydrocarbon Propellant)

Can	% Fill	Propellant	Cumulative Weight of Particles Below: (μm)									
			0.5	1.0	6.0	10	20	30	40	50	60	70
1	100	A-70	.13	.42	8.4	19.0	49.6	74.4	91.1	96.1	98.8	99.7
1	50	A-70	.04	.15	4.6	11.7	37.1	63.2	82.2	92.9	97.6	99.3
1	25	A-70	.09	.27	4.7	10.3	28.1	46.8	63.2	76.0	85.2	91.4
2	100	A-70	.18	.54	9.1	19.5	48.2	71.6	88.4	94.2	97.8	99.2
2	50	A-70	.10	.35	7.0	15.9	43.1	67.5	84.0	93.1	97.4	99.1
2	25	A-70	.21	.55	6.6	12.9	30.6	47.5	61.9	73.3	81.8	87.9
3	100	A-70	.07	.24	4.9	11.2	32.0	53.7	71.5	84.0	91.8	96.1
3	50	A-70	.14	.39	5.6	11.7	29.8	47.8	63.2	75.3	84.1	90.1
3	25	A-70	.04	.13	3.2	7.9	25.0	44.9	63.2	77.6	87.4	93.5
4	100	Aeropin-70	.30	.85	11.7	23.6	53.2	75.3	88.4	95.0	98.0	99.3
4	50	Aeropin-70	.26	.69	8.1	15.9	36.7	55.3	70.0	80.7	88.1	92.9
4	25	Aeropin-70	.16	.49	6.5	12.5	30.0	45.9	60.1	72.0	80.2	86.4
5	100	Aeropin-70	.20	.61	10.3	21.8	53.0	76.0	89.6	96.0	98.7	99.6
5	50	Aeropin-70	.25	.66	7.8	15.3	35.5	53.9	68.6	79.5	87.0	92.1
5	25	Aeropin-70	.05	.19	4.5	11.0	33.4	56.9	75.7	87.9	94.7	97.9
6	100	Aeropin-70	.18	.54	9.1	19.5	48.2	71.6	86.4	94.2	97.8	99.2
6	50	Aeropin-70	.20	.58	8.2	16.7	40.4	61.4	76.9	87.1	93.2	96.6
6	25	Aeropin-70	.41	.95	7.9	14.1	29.5	43.4	55.2	65.0	72.9	79.2
7	100	PIP-70	.40	.93	13.2	25.3	61.1	82.3	89.1	96.3	97.9	99.2
7	50	PIP-70	.33	.97	9.4	18.0	35.2	52.9	67.0	79.8	90.1	91.6
7	25	PIP-70	.14	.50	6.3	14.1	35.4	54.1	67.6	81.3	87.3	89.0

ing for about 4.6% of all European aerosols. During 1979 the Japanese production amounted to about 13 million pounds (6,500 metric tons), going into about 60 million cans.

DME was used by inventor Eric Rotheim of Norway as early as 1922 in preparing aerosol compositions. It was unavailable in the U.S.A. from several firms during the period 1950-1968, but then discontinued as a commercial item, although cylinder supplies could be ordered from specialty houses. In 1981 E.I. du Pont de Nemours & Co., Inc. entered the U.S.A. market with a highly purified material, made from a less purified form which they used internally as a reaction intermediate in the production of dimethylimide for making textile polymers. The price of DME during 1982 was \$0.57/lb. (\$1.26/kg) in bulk lots, f.o.b. plant.

In Europe, the West German firm of Union Kraftstoff, GmbH. decided to purify their DME for aerosol uses at the request of a Dutch filler, Aerofako by (AKZO), and this resulted in the 1966 introduction of the first DME aerosols: hair sprays, on the French market. With the recent expansion of the aerosol market for DME, Union Kraftstoff has increased the yield of their manufacturing process to provide a production capacity of up to 100 million pounds (45,400 metric tons) per year. The price of DME in Europe was said to be in the order of \$0.27/lb. (\$0.59/kg) in mid-1982.

DME is produced in Japan by four companies as a by-product of high pressure methanol synthesis. The market was said to have grown by 22% between 1979 and 1980, but supply is not viewed as a potential problem there. In Canada, production interest has been expressed by both CCL Industries Ltd. (Toronto) and Alberta Gas Chemicals Ltd. (Montreal). The latter currently is a producer of 99.85% methanol by high pressure synthesis in the province of Alberta. About 60% of the anticipated CCL Industries Ltd. production would be available for purchase.*

Purity and Physical Properties of DME.

The most effective manufacturing processes for DME begin with the reaction of bituminous or lignitic coals with steam to give water gas (CO, H₂, CH₄, etc.), which is then passed over finely divided nickel or an alternate catalyst at 660°F (350°C) and 450 psig (3.00

MPa) conditions to form formaldehyde, which is then reduced to methanol and a small amount of DME. Depending upon conditions, these last two products can be reduced by the hydrogen to form methane and water, but this is not allowed to occur to any significant extent. Where the reaction is adjusted to give methanol as the final product, only about 1.5 to 4.0% of DME is formed as a by-product. But by minimizing the steam content and changing other process conditions the output of DME can be increased, to as high as 40% of the total. The propellant can be considered to be formed by the dehydration of methanol.

The specifications for DME will vary depending to some extent upon the synthesis procedure, but more particularly upon the purification process. Specifications for European and U.S.A. products are given in Table XXXII.

In the presence of oxygen (or air) and ultraviolet light, DME will slowly form a rather unique peroxide: H₂C(OOH).O.CH₃. Since peroxides can be thermally or mechanically unstable, and have led to explosions in the case of diethyl ether and di-isopropyl ether, the significance of this reaction was studied in the case of DME. It has not been found to present a problem in either glass or metal containers, with DME alone or in formulated products. Conjecturally, this may be because ultraviolet radiation of a sufficiently short wavelength to cause peroxidation cannot penetrate the glass or metal dispenser.

Another potential concern was the generation of bichloromethyl ether (BCME), which is considered to

TABLE XXXII

Specifications for Dimethyl Ether (DME)

Specification	Du Pont	Union Kraftstoff
Organic Purity	99.8% min. 99.9% typ.	99.6% min. 99.8% typ.
Water	0.05% max.	0.05% max.
Methanol	0.02% max.	0.001% max.
Methane, ethane, propane & butanes		0.4% max. 0.2% typ.
Sulfur compounds		0.0001% max.*
Mineral oil		0.003% max.
Formaldehyde		trace**

*Private communication: 0.2 ppm is typical.

**Private communication.

Although not stated in specifications, traces of acetone, ammonia and acetic acid may be present in the 0.001% range.

*The firm prefers to use the terms dimethyl oxide or DMO for this product, feeling that the word *ether* has an unpleasant connotation of flammability, anesthesia and odor.

be a powerful carcinogenic compound. Some early data indicated 10 ppb of BCME in several aerosol formulas containing both DME and chlorinated compounds. However, later tests on formulas up to four months old showed no BCME, using special instrumentation with a threshold sensitivity of 1 ppb. In fact, inoculated BCME formulas showed anywhere from slow to rapid decomposition of the added compound, due to reaction with water, ethanol or other polar ingredients. No BCME was formed upon spraying DME/chlorocarbon formulas into ultraviolet irradiated air, even after an hour of aging time and under humidities ranging from 0 to 57%. In this study the instrument had a sensitivity of 100 ppt (100 pg/g). The suggested BCME carcinogen problem can thus be dismissed as fiction.

The physical properties of DME are provided in Table XXXIII. The propellant is a clear, water-white, virtually odorless liquid having a low viscosity and surface tension. It is unique among propellents in that it has a high solubility in water and functions as an excellent solvent for many other polar substances. See U.S. Patent 3,207,386 (Sept. 21, 1965).

TABLE XXXIII

Physical Properties of Dimethyl Ether (DME)

Formula	CH ₃ O·CH ₃
Molecular Weight	46.07
Vapor Pressure at 70°F (21.1°C) psig	63.03
Vapor Pressure at 130°F (54.4°C) psig	174.
Freezing Point	-217.3°F (-138.5°C)
Boiling Point	-12.7°F (-23.7°C)
Specific Gravity (liquid) at 68°F (20°C)	0.66
Specific Gravity (gas) at 68°F (20°C)	1.617
Air = 1	
Critical Temperature	231.6°F (126.9°C)
Critical Pressure	777.5 psig (5.361 MPa)
Critical Density (g/ml)	0.242
Flash Point	-42°F (-41°C)
Lower Explosive Limit (v% in air)	3.4
Upper Explosive Limit (v% in air)	18.2
Heat of Combustion (BTU/lb)	13.586
Auto-ignition Temperature	660°F (350°C)*
Solubility of Water in DME at 68°F (20°C) and 63 psig (w%)	5.84
Solubility of DME in Water at 68°F (20°C) and 63 psig (w%)	34.17
Solubility of DME in Water at 68°F (20°C) and 1 atm. (ml gas/ml)	36.5 ml/ml

*West German sources report 455°F (235°C). The difference may relate to the tester or testing conditions used.

Because DME is such a strong solvent, special precautions must be used in the selection of valve gaskets and crimping specifications. The formulator can have a lot of nasty surprises in these areas. Crimping specifications are suggested as 1.070 ± 0.005 " (27.18 ± 0.13 mm) for diameter and 0.182 " (4.62 mm) maximum for crimp depth, except in the case of the Precision PE-sleeve cup gasket, where the differences in geometry suggest a crimp depth specification of 0.185 ± 0.005 " (4.70 ± 0.13 mm).

In the case of stem gaskets, neoprene (with its low degree of hydrogen bonding capacity) is good unless the methylene chloride content of the formula exceeds about 25%. Buna is possibly the best from a weight loss standpoint, but even small additions of methylene chloride can be disastrous. The modified bunas used in Europe and to a small extent in the U.S.A. are very good and have less sensitivity to methylene chloride. Butyl rubbers are generally excellent, but are subject to a \$5.00/M upcharge in the U.S.A. Rather surprisingly, the Viton fluorinated polymers are extremely poor, often turning into a mush with significant concentrations of DME.

Cup gaskets also present a complex picture. GK-45 neoprene has fair resistance in the absence of methylene chloride, but weight losses increase to three or more times the normal rate when 20% of this solvent is included in formulations. The Precision PE-sleeve gasket is rated as excellent. A bit of weight loss may take place for a day or two, but then the PE seems to cold-flow and seal off any crevices or imperfections, so that further losses become quite low indeed. (This also occurs with other high-solvent formulations.)

Cup gaskets of the cut or pre-formed type show varied performance. Neoprenes are acceptable in general, but buna is good only where methylene chloride is absent. European studies have shown that the three common water-based cut gaskets are acceptable, as are some of the new laminated cut gaskets using buna/neoprene at different Durometers for optimum sealing. Viton cut gaskets are totally unacceptable.

Weight losses as low as 0.3g/yr have been reported for the combination of butyl stem gaskets and PE-sleeve gaskets under ambient storage using a 50% ethanol and 50% DME formulation. Replacing the PE-sleeve with a GK-45 gasket increased the loss to 0.5 g/yr. In the case of a higher solvent formulation: 10% petroleum distillate, 40% 1,1,1-trichloroethane, 20% methylene chloride and 30% DME, valves with butyl stem gaskets

and either PE sleeve, water-based flowed-in or various cut type gaskets gave ambient losses of 2 to 4 g/yr. With GK-45 this increased to 7 g/yr. In fact, the GK-45 gasket will give an unusually wide spread of individual container leakage rates with many DME formulas. In one sequence of 72 cans rates ranged from 0.4 to 73.4 g/yr.

In any event, the above information should be regarded as indicative only. Extensive weight loss studies should always be run, preferably using stem and cup gasket combinations suggested by the valve companies for the formulation type under consideration.

The toxicological profile of DME is very good. It has a low order of acute, subacute and subchronic inhalation toxicology. Chronic studies funded by du Pont are now in progress. In one key study, rats were exposed to as high as 20,000 ppm of DME for seven months. There was no gross, clinical or histopathologic evidence of toxicity, other than a 2% decrease in liver weight for rodents exposed at the highest DME level tested. There are no mutagenic or teratogenic effects, at least up to the tested limit of 28,000 ppm. The propellant is metabolized rapidly in the body.

It is a very weak cardiac sensitizer. In studies at two laboratories an effect level (EC_{50}) of about 200,000 ppm (20v%) in air was established.

After a review of the toxicological data to date, the Dutch government adopted a provisional no-effect exposure level of up to 10,000 ppm (1v%) for DME. The E.I. duPont de Nemours Co. has established an acceptable exposure limit (AEL) of 1,000 ppm for workers. Until the long-term, two-year inhalation studies are complete the company requires that their DME be used only where inhaled concentrations will

be very low. They will not offer the propellant for cosmetic and air freshener applications, for example. In Japan, where flammable propellents cannot be used for cosmetics or personal products by order of the Ministry of Health, a petition has been filed to allow the use of such propellents, provided the flame extension of the final aerosol product does not exceed 8" (20 cm).

DME is not of concern as a possible depletion agent for stratospheric ozone. The material is attacked rapidly by tropospheric hydroxyl radicals and nitrogen oxides under the influence of ultraviolet radiation. This accounts for about 99.9 + % of DME and an additional 0.02% or so is rained out into the aquatic environment. Somewhere between about 0.10 to 0.01% of the gas is thought to penetrate into the ozone layer some 10 miles (16 km) high, given a sufficient span of years, but even then no depletion-related reactions are expected to occur from this off-sourced contaminant.

Solubility Aspects of DME

The water solubility properties of dimethyl ether are quite unique. They have paved the way for the commercial introduction of certain water-based paints and are being studied for numerous other applications. In the formulation of polyurethane aerosols, the introduction of very minor amounts of DME acts to tie up traces of moisture that would otherwise affect adversely the long-term stability of the urethane pre-polymer. For example, without 2 or 3% DME many formulas will turn very viscous or even harden within about 6 to 12 months at ambient storage. With it, these same formulations have exhibited up to 30 months of good storage in tests conducted to date. (These data relate to aerosol units that have never been actuated. After an

TABLE XXXIV

Solubility and Pressure Development for DME and 25% P-152a/75% DME Mixtures With Water, Ethanol and 50/50 w% Solutions of Ethanol and Water

Pressure	DME Propellant			25% P-152a/75% DME Propellant		
	Water*	Ethanol	50/50 (W:E)	Water**	Ethanol	50/50 (W:E)
64	—	—	—	0	0	0
63	0	0	0	93 +	3	3
60	63	13	21	93	10	10
50	72	41	48	96	35	44
40	79	57	63	89	53	74
30	85	71	75	98 +	66	84
20	90	82	85	99	78	93
10	94	91	93	99 +	89	99
0	100	100	100	100	100	100

*Insolubility range: 6 to 34% water. (Blends over 6w% ethanol are miscible.)

**Insolubility range: 3 to 92% water. (All compositions over 27w% ethanol are miscible.)