

[Previous Page](#)

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.)

actuation, effects induced by the non-metallic valve components may cause strong increases in viscosity after 30 to 60 days.)

The water-ethanol-DME system is of particular interest. DME is soluble up to 35% in water. If 6% ethanol is added to any ratio of water and DME, complete solubility will occur. DME dissolves in water with the evolution of a fair amount of heat, indicating that strong bonding forces are involved. The physical affinity between the two is so intense that pressure builds up slowly as DME is added. Also, because of this same intra-molecular attraction, the particle size of the spray tends to be coarser than anticipated. By adding ethanol, these properties are diluted and the spray pattern improves.

Du Pont has recommended the use of P-152a ($\text{CH}_3\cdot\text{CHF}_2$) in conjunction with DME. P-152a contributes the pressure requirement while DME provides solvency and adds to the total percentage of propellant present. Both have about the same pressure and flammability levels (similar LELs) and this is a further benefit. The pressure properties of DME in ethanol, water, and ethanol/water (50:50 w%) solutions are compared with those of 25% P-152a/75% DME in the same solvents in Table XXXIV (Page 357).

DME is similar to ethanol in that its affinity for water is sufficient to cause a relative contraction in the density of its water solutions, compared with the theoretical densities. This is illustrated in Table XXXV.

The strong solvent powers of DME are beneficial in the formulation of cologne and perfume aerosols.

TABLE XXXV

Pressure and Density of DME Solutions in Water

Temperature = 70°F (21°C)

DME Content	Pressure		Density	
	psig	kPa	Theoretical g/ml	Actual g/ml
0%	0	0	0.999	0.999
5%	10	67	0.975	0.994
10%	19	135	0.953	0.986
15%	29	197	0.929	0.976
20%	38	264	0.907	0.966
25%	48	331	0.889	0.952
30%	57	393	0.871	0.935
35%*	63	434	0.852	0.905
40%*	63	434	0.833	0.894
60%*	63	434	0.769	0.820
80%*	63	434	0.724	0.746
100%	63	434	0.668	0.668

*An immiscible, two-phase solution is formed.

Essential oils contain heavy notes or fonds: resinous substantive ingredients that are easily precipitated upon the addition of apolar substances to the concentrate. This has posed problems in the case of hydrocarbon propellents, mostly resolved by using carefully screened perfume bases and a minimum level of propellant. With DME, even at rather high concentrations, the perfume ingredients remain soluble, providing a clean solution and a more balanced fragrance. The DME also helps lift or exalt the perfume notes. It allows the introduction of more water to the formula, if desired. It is also less flammable than the hydrocarbons and provides a lower flame extension plus greater relative safety, if a bottle is ruptured near a flame source. And finally, since it smells rather like ethanol (with which it is isomeric), DME fragrance products are said to have truer odors than those that use other propellents. During 1981 a well known multi-national marketer in Europe successfully launched a line of hydroalcoholic perfume and deo-cologne sprays, all based on DME.

Hydroalcoholic and water-based bathroom air freshener sprays containing DME have been sold successfully in several European countries for a decade. The cans are set in a frame attached to a wall surface and are activated with a pull cord or chain. Hydroalcoholic hair sprays containing up to about 15% water, along with 35% ethanol and 50% DME, have been developed and show fast drying times, essentially no curl retention problems, and flame projection test results of only 12" (300 mm), compared with 16" to 20" (400 to 500 mm) for the anhydrous hydrocarbon types. These products are now commercial in Europe.

Underlying all these product developments is the element of cost. Both ethanol and isopropanol are taxed and are thus very expensive in Europe. By using a larger amount of propellant (facilitated by DME) costs can be reduced since less alcohol is required. A similar rationale can be made for using more water, which (again) is facilitated by DME formulations. Typical prices in Holland at the beginning of 1981 were as follows:

DME: 0.66 Guilder/liter = \$1.293/U.S. gallon
= \$0.232/lb.

Ethanol: 8.00 Guilder/liter = \$15.50/U.S. gallon
= \$2.370/lb.

Isobutane: 0.50 Guilder/liter = \$1.00/U.S. gallon
= \$0.265/lb.

ture per gram of product has often been taken as a standard of flammability. Experimentally this is measured most often in a closed drum tester of 55 gallon (200 liter) capacity. For gas mixtures with no liquid components it has also been measured using a 4" i.d. × 32" high (100 mm i.d. × 813 mm high) Lucite tube fitted with a spark plug next to the head of a wooden match. The tube is partly evacuated (typically to 200 mm pressure) and then refilled with the desired partial pressure of test material, plus air back to atmospheric pressure. The tube is inverted several times, allowing three or four loose rubber stoppers to fall through the gas space to facilitate gas mixing, and the ignition source is then actuated to see if the gas mixture is flammable. This device, developed by du Pont, is useful in determining LEL and UEL values.

The LEL for DME is 3.4v% in air (86 g/m³), while that of a comparable propane/isobutane blend is about 1.95v% in air (53.6 g/m³). In the closed drum test the comparison is 14.7 g to LEL for DME to only 8.3 g for hydrocarbon A-63.

These relationships have significance in circumstances where aerosol products are totally discharged at one time, either during normal use (such as an indoor insect fogger) or by dispenser leakage or rupture. If substantially more product is needed to cause a possible fire, then that product is inherently safer.

A final flammability consideration is BTU content. Because DME has only 13,310 BTU/lb (755 K.cal/100 g) compared with a typical figure of 21,350 BTU/lb (1204 K.cal/100 g) for the hydrocarbon propellents, and because DME formulas often contain more water, they are generally much lower in BTU/lb or fuel content value. As an example of this, two typical hair spray formulations can be compared:

67% Ethanol Concentrate
8% Water
25% Propane/isobutane A-36
14,250 BTU/lb (808 K.cal/100 g)
35% Ethanol Concentrate
15% Water
50% Dimethyl Ether (DME)
11,450 BTU/lb (650 K.cal/200 g)

The formulations have essentially the same spray characteristics, wetness and other properties, yet the DME type has only 80.3% of the BTU/lb of the hydrocarbon version. This is of interest to warehousemen and

fire fighters, since the lower fuel content formula presents less of a potential fire hazard.

In summary, dimethyl ether is a highly interesting propellant, capable of doing many things better than the conventional propellents. It is destined for a greater role in European and Japanese aerosol products. If the price decreases in the U.S.A. and Canada, its utilization in those two countries should increase remarkably in the coming years.

Methylethyl Ether and Diethyl Ether

Methylethyl ether (CH₃.O.C₂H₅) has a boiling point of 45.7°F (7.6°C), a density of 0.697 g/ml at 70°F (21.1°C) and a pressure of 9.8 psig at 70°F (67.6 at 21.1°C). It is thus far a laboratory curiosity, commonly made by the method of Williamson, from ethyl iodide (C₂H₅I) and sodium methoxide (CH₃ONa) in yields of about 81%. If needed commercially it can be made by the dehydration of methanol and ethanol, although in much lower yield, since dimethyl ether and diethyl ether are large by-products. About 18w% of water can be dissolved in MEE under its own vapor pressure at 70°F (21.1°C). It has a pronounced ethereal odor. If MEE is ever commercialized other propellents will have to be added, since it does not have a vapor pressure sufficient for aerosol uses.

Diethyl ether (C₂H₅.O.C₂H₅) has a boiling point of 94.3°F (34.6°C), a density of 0.708 g/ml at 70°F (21.1°C) and an ability to dissolve 7.4w% water at 70°F (21.1°C). It is not a true propellant. DEE is available as a by-product of the preparation of ethanol by hydrating ethylene with sulfuric acid and water. It is also obtained in good yield by the reaction of Senderens: heating ethanol over alumina inoculated with iron (III) chloride, at about 500°F (260°C). The material possesses a very strong typically ether-type odor, recognizable by some people at concentrations below 1 ppm in air.

The only commercial aerosol use of DEE is in the preparation of engine starting fluids. A typical formulation might contain 0.5% lubricating oil, 90.0% DEE and 9.5% of carbon dioxide. Since DEE has the fairly unique ability to shrink valve elastomers, making crimp dimensions very critical if leakage is to be avoided, one or two marketers have elected to include very small amounts of methylene chloride in their products to help counteract the shrinkage problem. The odor of DEE can be smelled at the valve of any engine starting fluid aerosol by simply removing the protective metal cap.

Bis(difluoromethyl) Ether and Bis(trifluoromethyl) Ether

During 1977 W.R. Grace began promoting two compounds: the first is variously called bis(difluoromethyl) ether, sym-tetrafluorodimethyl ether, perfluorodimethyl ether and finally 6-FDME. They were proposed as non-flammable propellents having good solubility and free from any implication with the stratospheric ozone layer. They are made, rather expensively, by the electrolytic fluorination of dimethyl ether and the company holds several U.S. Patents covering this art. For the price to get under about \$2.00/lb. (1982 basis) the fluorination process would have to be done by means of reactions of a regular chemical nature, involving hydrogen fluoride.

Preliminary toxicology yielded good results, such as acute toxicity and erythmial tests on the monkey, five and ten day ingestion and irritation studies and a 90 day inhalation test. Results of the Ames mutagenicity test were negative.

4-FDME and 6-FDME exhibit physical properties as shown in Table XXXVII.

By adding 10% 6-FDME to 4-FDME the vapor pressure is elevated from 20 psig to 36 psig at 70°F (138 to 248 kPa at 21.1°C), and by adding 25% of 6-FDME a pressure of 50 psig at 70°F (348 kPa at 21.1°C) is attained. 4-FDME has a strong affinity for such polar solvents as water and ethanol; a 50% 4-FDME and 50% ethanol (95v%) solution has a pressure of only 5 psig at 70°F (35 kPa at 21.1°C). These propellents dissolve significant amounts of such items as propylene glycol, dibutyl phthalate and sorbitan trioleate. They do not swell diptubes, but may extract the black colorants from exposed buna rubbers, as in glass aerosol valves. In summary, there are no commercial plans for these potentially useful propellents as yet, largely due to the cost of completing the toxicological profile and the cost of the materials themselves.

The Compressed Gases

The compressed gas propellents are generally considered to consist of carbon dioxide (CO₂), nitrous oxide (N₂O) and nitrogen (N₂). Theoretically the field is much larger and also includes ethane (C₂H₆), which was described earlier, argon (A), helium (He) and difluoromethane (CH₂F₂). However, these latter gases do not have any commercial aerosol applications in the pure form and are therefore not usually discussed.

The term "compressed gas" is denoted by the industry to mean a high pressure propellant that must be injected into containers in the gaseous form instead of as a liquid under pressure. This is in marked contrast to the regulatory definition, as set forth by the Department of Transportation (DOT) and various agencies, and which is supported by the Compressed Gas Association (CGA) and other standard-setting groups. According to the DOT, a compressed gas is, "Any material or mixture of materials having in the container either an absolute pressure exceeding 40 psi at 70°F or an absolute pressure exceeding 104 psi at 130°F, or both, or any liquid flammable material having a Reid (ASME Test D-323) vapor pressure exceeding 40 psi-absolute at 100°F." From all this it is possible to have a substance defined as a compressed gas, even if it exerts a pressure as low as about 4 psig at 70°F (27 kPa at 21.1°C), provided it is flammable.

The aerosol technologist presently considers that the "liquefied propellents" are those which can be shipped by ordinary tankcar and tanktruck, and thus have pressures equal or less than that of Polymerization Grade propylene; e.g. 156 psig at 70°F (1.076 MPa at 21.1°C). These gas liquids can be added to aerosol dispensers by standard T-t-V or U-t-C gassing techniques. Probably the highest pressure example of such propellents that has been filled to date is a blend of 4w% ethane and 96w% propane with a pressure of 128 psig at 70°F (883 kPa at 21.1°C). At pressures above

TABLE XXXVIII

Properties of Sym. Tetrafluorodimethyl Ether and Perfluorodimethyl Ether

Property	Sym-Tetrafluoro-Dimethyl Ether	Perfluoro-Dimethyl Ether
Formula	(CHF ₂) ₂ O	(CF ₃) ₂ O
Molecular Weight	118	154
Vapor Pressure (psig at 70°F)	20	217
Vapor Pressure (psig at 100°F)	54	345
Freezing Point - approx. (°F)	-240	-240
Boiling Point (°F) (1 atm)	28.4	-67
Vapor Density at Boiling Point (g/ml)	0.005304	0.011733
Density of Liquid (70°F) (g/ml)	1.3	1.4
Flammability	None	None
Hydrolysis in 1% NaOH Solution (80°F)	None	None

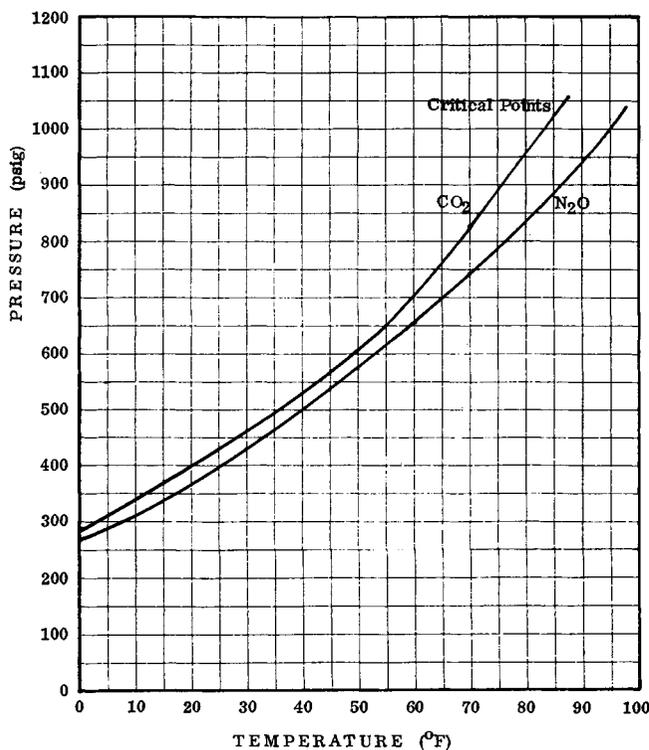


Figure 24. Pressure of CO₂ and N₂O Propellents at Various Temperatures

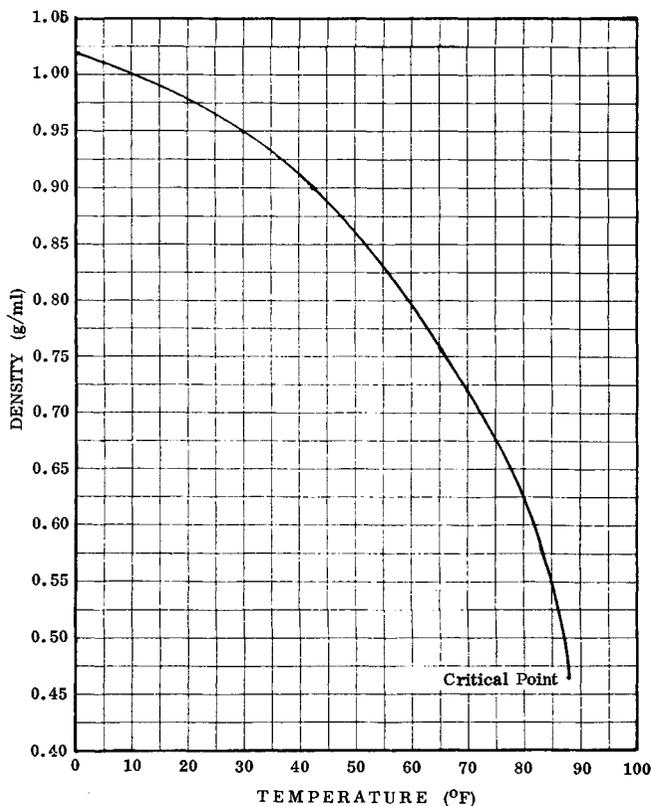


Figure 25. Density of CO₂ Propellant at Various Temperatures

this, end-buckling of tinplate cans could occur, especially under warm gassing conditions.

From all this we can suggest that the "aerosol compressed gas" category embraces gases with pressures higher than about 135 to 155 psig at 70°F (930 to 1068 kPa at 21.1°C), and which must be gassed into containers by gasser-shaker, pre-saturation gassing, T-t-V instantaneous impact gassing (with an appropriate valve design) or U-t-C instantaneous impact gassing methods. The term "fixed gas" or "permanent gas" relates to those gases such as nitrogen, helium and argon that are always gaseous (never liquid) at ambient temperatures. These are older terms, now rarely encountered.

The physical properties of several aerosol compressed gases are indicated in Table XXXIX.

The compressed gases were the first aerosol propellents, CO₂ having been used as early as about 1840 in the pressurization of certain milk products. Since then CO₂ and N₂O have been used in a number of food products, such as whipped creams, ice cream toppings, fruit flavored concentrates for addition to water or milk, chocolate milk concentrates, salad dressings, meat sauces, simulated butter sprays, popcorn sprays, garlic sprays, squirt-type drink mixes (such as in the home bar compounding of Manhattans or Daiquiris) and even an experimental pancake batter. Outside the food field, CO₂ is used often in such diverse products as starting fluids, bug killers, stain repellents for upholstery, disinfectant/deodorants, engine cleaners and windshield de-icers.

Since both CO₂ and N₂O have significant solubility in water, they can be added to foam products to destabilize the foam to various degrees. For instance, if nitrous oxide is added to a standard shave cream, the foam structure at the surface of the puff will "melt" to give an enhanced, pearly appearance. When the gases are added to various hydrocarbon-propelled cleaning products, the stability of the foam layer decreases and it is more readily absorbed into the cleaning cloth, rather than just being pushed around without significantly wetting either the cloth or the surface. The addition of about 50 psi (345 kPa) of nitrous oxide is usually sufficient. Conversely, a chocolate flavored ice cream topping propelled with nitrous oxide displayed surface darkening of the foam structure after a minute or so, and this was quite obvious by contrast when the topping layer was spooned, exposing the lighter product below. By the addition of a water insoluble propellant, such as

Freon FP-C-318 or Freon FP-115, at about 1%, the foam was stabilized and the problem resolved.

The foam destabilizing properties displayed by CO₂ and N₂O can be duplicated and even exceeded by other propellents showing water solubility, as well as by the addition of ethanol, isopropanol, glycol monomethyl ether (methyl cellosolve), silicone antifoams and other specific chemicals according to need. To get to the so-called quick-breaking foam stage a significant amount of co-solubilizing material is usually needed. About 25% of either dimethyl ether or ethanol may be sufficient, especially if a water soluble propellant such as CO₂, N₂O or P-152a can be included also.

The compressed gases have high pressures, actually far beyond the strength of ordinary aerosol cans. The pressure-temperature curves for both CO₂ and N₂O are shown in Figure 24.

The related density-temperature curve for CO₂ is shown in Figure 25, and the curve for N₂O (not shown) is almost identical to it at ambient temperatures.

Because of the high pressure characteristic, solubilities of these gases must be expressed as a function of both pressure and temperature. As the gases are added,

the pressure increases linearly with concentration, starting with that of the original contents as a baseline. This concept is quite accurate to about 200 psig (1.380 MPa), and thus covers all aerosol applications. Up to 200 psig (1.380 MPa) of CO₂ and N₂O have been added to a number of pure substances and several solutions without causing phase separations. The miscible status of barely miscible solutions might be altered by additions of these gases, but this has not been tested. In some cases considerable heating accompanies the introduction of CO₂ (and to a lesser extent N₂O) into certain solvents, such as ethanol and acetone. At least some heating (the Joules Effect) occurs for almost every solvent tested. Except in the case of water, where CO₂ reacts to form carbonic acid, the usual compressed gases do not combine chemically with aerosol ingredients.

The solubility relationships of CO₂, N₂O, N₂ and other gases have been described classically using such concepts as the Ostwald Solubility Coefficient, mol% solubility per atmosphere of partial pressure and so forth. In order to convert between the OSC (λ) and the weight of gas filled into an aerosol container under a set

TABLE XXXIX

Physical Properties of Certain Compressed Gas Propellents

Property	Carbon Dioxide	Nitrous Oxide	Nitrogen	Helium	Argon
Formula	CO ₂	N ₂ O	N ₂	He	A
Molecular Weight	44.0	44.0	28.0	4.0	39.9
Vapor Pressure (psig 70°F)	830.	745.	na	na	na
Freezing Point (°F)	-69.9*	-131.5	-345.93	-456.1	-326.6
Boiling Point (°F)	-109.2**	-127.26	-320.44	-452.0	-302.6
Specific Gravity (liq.) (70°F)	0.721	0.720	na	na	na
Specific Gravity (gas) (70°F) Air = 1	1.530	1.530	0.971	0.138	1.383
Density (gas) g/l 32°F 760 mm	1.9768	1.977	1.258	1.176	1.793
Density (solid) (-109.2°F)	1.561				
Critical Temperature (°F)	87.80	97.7	-232.6	-450.2	-187.6
Critical Pressure (psig)	1056.	1052.	491.5	33.2	704.2
Critical Density (g/ml)	0.468	0.457	0.311	0.0693	0.531
Flash Point (°F)	none	none	none	none	none
Explosive Limits in Air	none	none	none	none	none
Solubility in Water (ml/100 ml water at 32°F)	179.7	130.52	2.35	0.97	5.60
Solubility in Water (ml/100 ml water at 70°F)	85.4	69.62	1.51	1.02	3.0

*At 76.3 psig (526 kPa).

**Sublimes.

of experimental conditions we can use the equation of Hsu:

$\lambda X = (WRT/V_cMP) + (X - 1)$, where:

λ = Ostwald solubility coefficient (OSC)

X = Volume of liquid divided by volume of the container

W = Weight of compressed gas added (g)

R = Gas constant (82.06 ml-atm/mole-°K)

T = Temperature (°F)

V_c = Volume of container (ml)

M = Molecular weight of compressed gas

P = Total pressure (atmospheres, absolute)

Such concepts seem bulky and academic to the aerosol chemist, and they pose some rather lengthy translational difficulties for those who must consider solubilities in the more pragmatic framework of grams

per can. In formulation work, a result based on theory would be checked experimentally in any event, to avoid possible errors or inaccuracies.

A more practical guide has been developed, using air-free 202 × 509 aerosol cans (287 ml) filled to 80v% of capacity (230 ml) with various pure solvents or propellents. The weight of CO₂ or N₂O required to produce a pressure of 100 psig at 70°F (690 kPa at 21.1°C) was then determined. It was recognized that the 20v% head space would contain a portion of the gas; actually 0.0139 g/ml, or 0.792 g/can, and that this could be a very important percentage of the total gas weight if the solvent or propellant could dissolve only a small percentage. The data provided in Table XL shows the results of this study.

To be more exact, as gas is added the liquid volume swells, by about 1.3 ml per gram of CO₂ or N₂O, and

TABLE XL
Solubility of CO₂ and N₂O in Certain Aerosol Liquids and Propellents

Solvent	Gas	Solvent Weight Per Can (g)	Gas Wt. To Reach 100 psig at 70°F (g)	Gas Wt. Required to Reach 100 psig at 70°F			70°F	Pressure (psig)	
				(w/w %)	(g/100 ml)*	(g/100 ml)**		100°F	130°F
Isobutane	N ₂ O	128.1	10.17	7.33	4.42	3.98	100	143.5	—
	CO ₂	129.3	7.25	5.31	3.16	2.82	100	141.0	—
n-Butane	N ₂ O	133.5	11.26	7.78	4.90	4.44	100	141.0	—
	CO ₂	133.5	7.81	5.52	3.40	3.04	100	134.5	—
Odorless Min. Spirits	N ₂ O	170.5	9.76	5.41	4.25	3.71	100	125.5	151.5
	CO ₂	170.5	6.27	3.46	2.73	2.36	100	122.0	142.0
Water	N ₂ O	229.2	1.68	0.729	0.733	0.392	100	135.0	174.0
	CO ₂	229.7	3.50	1.500	1.524	1.224	100	140.0	182.0
Ethanol (100%)	N ₂ O	177.7	10.80	5.73	4.70	4.32	100	136.0	175.0
	CO ₂	177.6	10.48	5.57	4.56	4.18	100	136.0	172.5
Isopropanol (99.5%)	N ₂ O	176.4	9.46	5.10	4.11	3.59	100	124.5	152.0
	CO ₂	177.2	7.95	4.30	3.46	3.19	100	122.0	146.0
Acetone	N ₂ O	180.1	20.31	10.13	8.83	7.91	100	133	—
	CO ₂	179.1	24.06	12.08	10.45	9.22	100	143	—
Dimethyl Ether	N ₂ O	151.9	19.65	11.48	8.54	7.65	100	—	—
	CO ₂	151.7	17.75	10.46	7.72	7.03	100	—	—
Methylene Chloride	N ₂ O	301.0	20.25	6.31	8.80	7.87	100	136	—
	CO ₂	300.5	16.92	5.34	7.37	6.73	100	135	—
1,1,1-Trichloroethane	N ₂ O	296.4	16.90	5.40	7.35	6.71	100	131.0	—
	CO ₂	296.5	13.35	4.32	5.80	5.40	100	132.5	—
P-11 (CCl ₃ F)	N ₂ O	357.4	18.50	4.92	8.05	7.21	100	136.0	179.5
	CO ₂	355.8	13.00	3.53	5.65	5.26	100	135.5	176.0

*Of solvent; e.g. gas weight divided by 2.30. (Discounts head space gas.)

**Of solution. Excludes head space gas, figured at 0.000139 g/ml/psig of N₂O or CO₂ partial pressure, at 70°F.

this makes the head space smaller. In the case of aprotic solvents, such as acetone and dimethyl ether, there is a contractive effect due to intermolecular forces and the volume growth then diminishes to only about 1.0 to 1.1 ml per gram of dissolved gas.

A quick survey of Table XL would suggest that acetone is the strongest solvent listed. But it must be remembered that in the case of dimethyl ether, the gas pressure is built upon a base of 63 psig at 70°F (434 kPa at 21.1°C), and that by the time sufficient CO₂ or N₂O is added to reach 100 psig (689 kPa) the amount dissolved is already 76 to 97% as great as in acetone, resp.

The spray pattern reflects the level of CO₂ or N₂O in the formula. A volatile solvent also contributes to a finely particled spray. For instance, a 12% solution of CO₂ in acetone sprays like a dry gas, and a solution of 6.0% CO₂ in equal parts of acetone, methylene chloride and odorless mineral spirits (OMS) gives a very fine spray, like an anhydrous air freshener.

A 5% solution of CO₂ in anhydrous ethanol gives a spray considered marginally too wet for hair spray use. However, 6.4% solutions are considered satisfactory, although pressures are too high for tinplate cans. The addition of volatile solvents, such as methylene chloride (up to 20%) or isopentane (to 15%) act to bring the particle size of 5% CO₂ hair sprays into a good range.

A 4.0% solution of either N₂O or CO₂ in vegetable oil (usually with traces of carotene dye and butter flavoring) makes a very coarse spray suitable for spraying popcorn and even bread slices in institutional kitchens. A similarly coarse spray is obtained with 3.0% CO₂ and various odorless or low-odor petroleum distillates, for such products as bug killers and engine degreasers. Finally, there are sprays so low in gas that the only break-up is afforded by using a mechanical break-up valve. They include a commercial line of pet sprays, where the concentrate is about 95% water and where only 0.39% of dissolved N₂O is the sole propellant. These sprays are soundless, or almost so, and as such they do not startle pets when actuated.

A major concern with CO₂ and N₂O products involves the inevitable pressure drop during use, as propellant escapes from the liquid phase to enter the enlarging head space. For example, a product very high in ethanol and containing 5% CO₂ starts out at a typical pressure of about 90 psig at 70°F (621 kPa at 21.1°C), and during use this pressure dwindles to about 49 psig (338 kPa). due to frictional factors, the delivery rate only drops by about 25 to 30% during this time,

and this goes unnoticed by the consumer. In general, the pressure drop aspect has been over-emphasized, along with the concomitant factors of slower delivery rate and a coarsening of the spray. In development, aerosols made at the low end of the pressure specification should be tested for spray acceptability by spraying down to emptiness. Also, vapor valves should never be used, and special care should be taken to assure crimp reliability. Crimp leakage has been more of a problem with CO₂ and N₂O formulas than others (especially ethanol types). This is due to the high pressures in the can and the fact that these gases are very small molecules, and thus are better able to wriggle through elastomeric seals than the much larger hydrocarbons and fluorocarbons. Only a few grams of propellant loss can have a significant effect upon the product quality. Cans containing both methylene chloride and CO₂ and held in upright storage have been checked for both pressure and weight loss after a year, with the finding that over half the weight loss consisted of methylene chloride. Similar results were obtained with 1,1,1-trichloroethane, although loss rates were only 10 to 20% of the methylene chloride packs.

Nitrogen gas has been used to pressurize concentrates to be delivered as streams or as very coarse sprays produced by a mechanical break-up valve. One interesting use is the wasp and hornet spray. The concentrate is predominantly a C₁₀H₂₂ type deodorized kerosene, pressurized with about 0.3% N₂ to 100 psig at 70°F (689 kPa at 21.1°C). With the proper valve a stream can be projected up to about 16 to 20 ft (4.9 to 6.1 m), which provides a better range and enhances operator safety, although attacking wasps sometimes fly back along the stream to sting the user. When such products are formulated using CO₂, sufficient break-up occurs that they are virtually unusable beyond about 6 or 7 ft (2 m).

Nitrogen has been used to pressurize toothpaste in non-compartmented aerosol units, probably now obsolete, although on the market for up to about ten years. When used to pressurize food items such as honey or pancake syrups, the product can be dispensed looking like it usually does, but after a second or two it undergoes a metamorphosis, turning translucent, then milky as the nitrogen forms ever larger gas bubbles in the liquid matrix. Eventually, in perhaps ten or twenty seconds, the gas rises to the surface and escapes, leaving a normal product. This would probably be "too much magic" for the consumer, and such products have never entered the market except in very small numbers.

Toxicological Considerations; CO₂ and N₂O.

The toxicology of CO₂ is well defined. It is present in normal air at about 300 ppm, so it is obviously compatible with life forms. CO₂ functions as a regulator of the breathing function, and an increase will accelerate the rate of breathing. At 0.1 to 1.0% levels there is a slight but unnoticeable increase, while at 2% there is a 50% increase, and at 3% a 100% increase. At 5% the increase rises to 300% and breathing becomes laborious. A level of 10% CO₂ can be endured for only a few minutes. From 12 to 15% soon causes unconsciousness and 25% will cause death in several hours. The threshold limit has been established at 5000 ppm (0.5%). The gas has a pungent odor, sharp and acidic, but not unpleasant. The solid form (dry ice) can cause severe frostbite.

The toxicology of nitrous oxide has been studied exhaustively. It is well recognized as a medical and dental anesthetic, the so-called "laughing gas" being a mixture of about 80% N₂O and 20% O₂. Various studies suggest that chronic exposure can cause a number of effects, particularly on frequently dividing cells. They are time and dose dependent. They impair vitamin B₁₂ metabolism and the production of tetrahydrofolate, which can affect DNA synthesis. Symptoms of sub-chronic exposure include early sensory complaints, loss of balance, leg weakness, gait ataxia, impotence and sphincter disturbances. Changes have been seen in lysosomal lung cells in mice, and damage has been found in the cortical cells of rats. Epidemiologic work has uncovered higher risks of spontaneous miscarriage, liver disease and other serious health problems. A number of deaths have resulted from deliberate deep inhalation, a drug abuse form designed to provide a psychedelic experience but also leading to intoxication, autolethal acts and often simple asphyxiation. Exposure of pregnant rats to N₂O showed it to be fetotoxic and a teratogen. The mechanism was not related to the intrinsic mechanism for anesthesia. Xenon gas, a very similar anesthetic, was without effect on the rats.

While these toxicological findings may seem a bit grim, and might be sufficient to cause the cancellation of development work on some new propellant, the controlling factor is that about 600,000 clinical and hospital personnel and over 100,000 dental personnel work with the gas during many days each year and yet have suffered no ill-effects. N₂O exposures at aerosol filling

plants should be far less, and the consuming public would have virtually no exposure at all. It is fortunate that the epidemiological 100 year history of safe use far outweighs the concerns relating to the effects of high-level repeated exposures.

Nitrogen (and helium and argon) propellents are probably used in fewer than 1 to 2 million aerosol units per year in the U.S.A., and they are formulated at very low levels, generally in the range of 0.1 to 0.5% of the product. There are no toxicological constraints other than the obvious but remote possibility of asphyxiation in a grossly misengineered and mismanaged production setting.

Production Aspects of CO₂, N₂O and N₂ Gases

CO₂ is available as the liquefied gas in either 60 lb (27.2 kg) net cylinders or in tankwagons of varying capacities. The Commercial Grade product contains 99.5% min. CO₂, plus 0.342% max. N₂, 0.086% max. O₂ and 0.072% max. H₂O. Although "bone dry" grades and even purities of up to 99.995% CO₂ are also available at a price, virtually all fillers use the Commercial Grade product.

Banks of interconnected cylinders can be purchased for smaller operations, but otherwise the so-called "CO₂" receptacle" is recommended. It consists of an insulated horizontal bulk tank bolted to a frame that also carries a refrigeration and heating system. Between the two, the propellant is maintained at $2 \pm 4^\circ\text{F}$ ($-16.7 \pm 7.2^\circ\text{C}$) and this keeps the CO₂ pressure at 300 ± 20 psig (2.069 ± 0.140 MPa). Between productions the refrigeration unit operates periodically to keep the liquid sufficiently chilled. During productions, as gas is withdrawn from the top area of the tank a cooling of the liquid phase takes place due to evaporative replacement. When the pressure drops to the base of the established range, a relay turns the heating system on to restore the mid-point temperature.

For cylinder banks evaporative cooling can be more of a problem. If nothing is done to rewarm them the liquid CO₂ will drop to about -40°F (-40°C) and there will then be insufficient pressure generation to continue the production function. Also, the cylinders will quickly develop a thick coating of ice. To prevent all this, a person should frequently spray the banks with warm water from a hose.

Nitrous oxide can be purchased in up to a 99.99% ultra high purity grade, and also in a 99.93% medical grade, but the Chemically Pure Grade at 99.0% min.

N_2O is almost always sufficient. The main impurity is nitrogen. N_2O is normally made by the thermal decomposition of ammonium nitrate (NH_4NO_3). Any entrained powder and traces of reactive nitrogen oxides are removed by dissolution in water, after which the purified gas is dried and stored.

N_2O may be used out of the same type cylinders (60 lbs net, or 27.2 kg) and the same receptacles as were described above for CO_2 . All conditions and comments apply equally to N_2O operations.

Unlike CO_2 , nitrous oxide is a strongly endothermic gas. Heat is absorbed when it is theoretically formed from the elements. The standard heat of formation (ΔH_f°) is 19.49 kg-cal/mol. Although it is essentially unreactive at ambient temperatures, it becomes increasingly active when heated. At above about 450°F (232°C) it functions as a strong oxidant. Recognizing this, any frictional or other heating should be stringently avoided if there is any chance that combustible material may be present, such as lubricating oils or greases.

In one memorable occasion a 3/4-inch (19 mm) i.d. steel pipe, carrying 300 psig (2.07 MPa) N_2O from a receptacle to a gasser-shaker machine suddenly became red hot at the midsection, just below the ceiling of the gas house. Within another 15 seconds or so it became white hot and then melted, with the released gas jet blowing molten globules of steel in all directions. In another instance, a solution of N_2O in methanol (CH_3OH) at about 200 psig (1.38 MPa) pressure caused a relatively small pre-saturation tank to detonate in the premises of a Chicago area filler, causing severe consequences. And finally, N_2O managed to slowly decompose to N_2 and O_2 when packed in aerosols with a relatively acidic food condiment, causing cans to explode several months after filling. The product, called "Sizzle Spray", was abruptly discontinued. These three episodes, along with many others, have never been satisfactorily explained. It is known that N_2O decompositions are very sensitive to catalysis, and that once initiated on a micro scale they might produce a hot spot that might rapidly enlarge. Catalytic actions might be the key to these mysterious occurrences.

During the early days of the aerosol industry CO_2 , N_2O and their mixtures were injected into sealed cans backwards through the valve, using in-line gasser-shaker equipment, such as the LeMay Machine Co.'s 8 to 11 station machines. The rate of gas addition was a function of the smallest orifice size in the valve, the

pressure differential between inlet line and can, the viscosity of the product, the fill volume and the selection of gas. For instance, N_2O usually dissolves more slowly than CO_2 , and with less heat of solution. The shaking efficiency depended, in part, upon the relative size of the head space. If the head space was less than about 16v% (or even 20v% for less fluid products) the gassing time was lengthened because the liquid could no longer be agitated so violently. As of this writing, gasser-shakers are still used widely. They extend from the small, semi-automatic types such as that made by L'Air Liquide, S.A. of France, rated at 8 to 16 cpm, to the advanced 6, 12 and even 18-head rotary types, such as those offered by Andora Automation, Inc., which are capable of speeds up to 160 cpm, depending upon conditions.

During the late 1950s in the U.S.A. Kartridg Pak, Inc. developed a pre-saturation method for adding these gases. Considering a typical bug killer for example, consisting of 2% toxicants, 95% petroleum distillate and 3% CO_2 , a pre-mix of about 47 parts petroleum distillate and 3 parts CO_2 was prepared in a pressure-resistant, baffled, mixing vessel of about 20 to 60 gallon (75 to 227 liter) capacity. The petroleum distillate was maintained at a volume level, and the CO_2 was added using a supply line fitted with a pressure regulator which, in this case would be set at about 185 psig (1.276 MPa). After filling the can with 2 parts toxicants and 48 parts petroleum distillate, an equal weight of the pre-mix would be added, using T-t-V or U-t-C propellant gassing techniques. The final can pressure would be about 88 to 90 psig (607 to 621 kPa). The small apparent loss of pressure would actually relate to the fact that the pre-mix was only about 98% saturated, and would also provide gas for the head space of the aerosol can. A schematic diagram is shown in Figure 26 (Page 368).

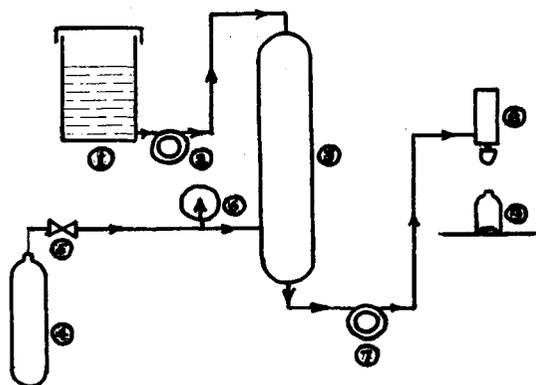
The final injection method, known as instantaneous impact gassing, is undoubtedly the best procedure available, provided the concentrate is reasonably fluid; e.g. about twice as fluid as corn oil. The gas is brought to either the T-t-V or U-t-V gasser under a pressure of typically 625 psig (4.31 MPa) and a fixed volume is rammed into the can at great speed. Before the pressure in the can is able to rise to critical values, the liquid is blasted into a fine mist so that it can absorb the injected gas almost completely. If the process is conducted correctly, the excess pressure (that amount over the equilibrium pressure) will only be about 10 psi (69

kPa), and it will subside completely in a day or two. A term called Impact Gassing Efficiency relates to this pressure difference:

$$\% \text{ IGE} = \frac{\text{Equilibrium Pressure}}{\text{Actual Pressure}} \times 100\%$$

The contents temperature must be the same when measuring both pressures. As a part of the procedure for Actual Pressure determination the can temperature should be measured using a thermistor probe of the "skin temperature" profile. Because of the Joules Effect, measuring the concentrate temperature prior to gas injection will give low temperature results.

If the %IGE is below about 80%, the system should be examined. The head space may be too small for adequate agitation. The valve cup wall (in U-t-C operations) may overly concentrate the ram-jet effect of the entering gas, causing different degrees of concentrate break-up. The material may be too viscous, the valve (in T-t-V operations) may not allow ultra-quick entry of the gas into the can, the pressure may be too low, or various settings on the U-t-C may be incorrect. When



1. Product to be packaged in aerosol form. (In this scheme 100% is pre-pressurized.)
2. Transfer pump.
3. Saturator.
4. Compressed gas supply.
5. Pressure regulator.
6. Pressure gauge.
7. Excess pressure pump.
8. Metering pump, or gasser.
9. Aerosol container.

Figure 26. Pre-Saturation Equipment for the Addition of CO₂ and N₂O to Aerosols

everything is functioning smoothly, rates as high as 288 cpm have been obtained using a re-engineered Kartridg Pak 9-head U-t-C gasser with cans as large as the 211 × 713 size.

Methylene Chloride

With a boiling point of 103.55°F (39.75°C) methylene chloride is not a true propellant, but functions more as a propellant adjuvant or extender. The 1981 production of 545 million pounds (247,000 metric tons) in the U.S.A. was expected to drop to 530 million pounds (240,000 metric tons) in 1982. The major end uses consist of paint removers (30%), aerosol propellents (20%) and degreasers (10%), and this 106 million pound (48,000 metric ton) aerosol propellant market is expected to remain about flat to very slightly upward in the next few years.

The price of methylene chloride (inhibited) was listed at \$0.305/lb (\$0.673kg) at the beginning of 1982, but with a domestic capacity of up to about 825 million pounds (375,000 metric tons) there is great downward pressure on pricing. Imports were 60 million pounds (27,000 metric tons) in 1981, causing still further price problems.

Other properties of methylene chloride include, M.W. = 84.94, Freezing Point = -139°F (-95°C), density = 1.3255 g/ml at 20/4°C and water solubility = 2.0% at 70°F (21.1°C).

Because of early concerns expressed by the Food and Drug Administration (FDA), the toxicology of methylene chloride has been examined exhaustively. To repeat the total of this work, using 1982 prices, would cost in excess of \$20,000,000. The industry position is that methylene chloride should pose no significant hazard to health or the environment when used within established guidelines, according to all animal and human toxicology data now available. Perhaps the key element in the entire battery of about two dozen programs is the massive study, cosponsored by Diamond Shamrock, Dow Chemical Co., Imperial Chemical Industry (U.K.), Stauffer Chemical Co., and Vulcan Materials. The study, conducted by Dow Chemical Co., involves a two-year inhalation of methylene chloride vapors at concentrations of 500, 1500 and 3500 ppm in air by hamsters and rats of both sexes. The test results are based on examination of 90,000 tissue samples taken from 1,896 animals. The final compilation of results shows no increase in malignant tumors in the hamsters and female rats, and only a slight in-

crease in the male rats at the highest solvent level tested. This last finding does not indicate significant risk of cancer or other known adverse health effects when methylene chloride is used according to accepted exposure guidelines. The LD₁₅ orally in rats is 1.6 ml per kg. It is a narcotic to humans in high concentrations.

Methylene chloride is used in aerosol formulations, generally at levels of below about 25%, although levels to 35% are known in some coating products. An insecticide made in Holland is known to contain about 72%. At above 20% or so, some rather difficult containment problems may occur, simply because methylene chloride is such a strong solvent and can easily cause swelling and penetration of elastomeric seals. Buna gaskets have the lowest resistance, and neoprene types should be used at over about 20%. Considering the aspects of solubility parameter (See Table XXIII) and so forth, neoprene should be affected almost as drastically as buna gaskets. But neoprene is such a dense, tough material that it resists deformation and consequent permeation.

Neoprene stem and mounting cup gaskets should be used for products having more than about 20 to 25% methylene chloride. Although weight losses are often five to ten times higher than for non methylene chloride formulas they successfully hold compositions containing as high as 80% of the solvent, provided storage temperatures do not exceed about 104°F (40°C) and a good, tight crimp is applied. Dimensions of about 1.075" crimp diameter and 0.175" crimp depth are recommended.

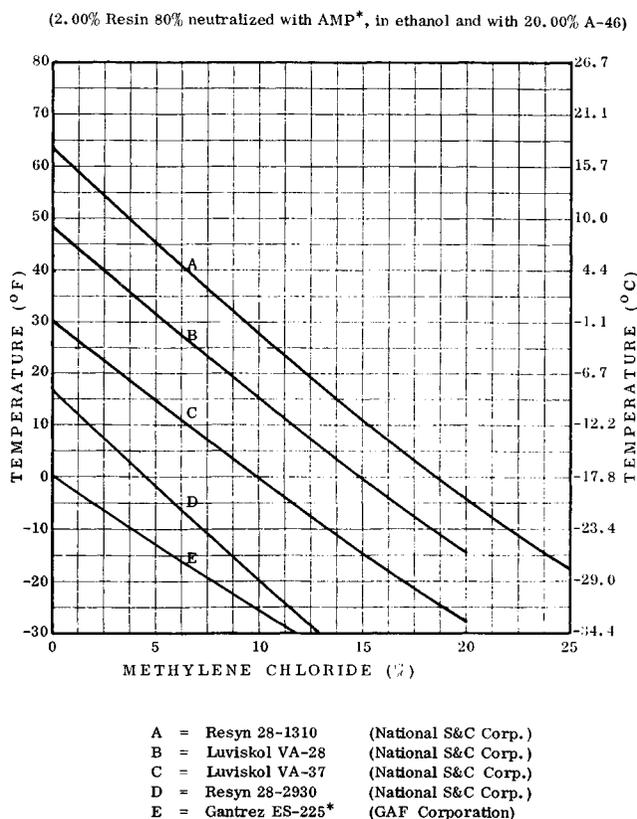
The best valve seal for methylene chloride is Viton, but the very high expense tends to limit its use. Valves with Viton stem gaskets and neoprene-based flowed-in gaskets have been successful with insecticide and paint stripper formulas containing as high as 70 to 80% methylene chloride, even at temperatures to 120°F (49°C), although occasional gross leakers may be encountered, even under ideal crimping conditions. Even better performance can be obtained where both the stem and cup gasket are composed of Viton. However, Viton cut gaskets for valve cups are so costly that this ultimate approach is almost never used in practice. Weight loss data for a high methylene chloride insecticide formula are given in the chapter on Crimping.

The use of methylene chloride in cosmetic products has been banned in some countries, and limited to 35% or other percentages in others. In the U.S.A. and Canada there are no limitations, nor are any being considered. Hair sprays constitute the largest cosmetic

product containing methylene chloride, with the solvent incorporated into quite a large number of formulas, generally in the range of 12 to 24%. Consumers start to pick up the solvent odor and skin tingling effects at over about 16%, but they do not develop any purchasing resistance until solvent levels over 20% are used. Many hypo-allergenic persons cannot use methylene chloride hair sprays without developing edema, rash or other irritations of the scalp and adjacent skin surfaces.

For the manufacturer, methylene chloride facilitates the production of hair sprays by speeding the dissolution of several important film-forming resins that are sold in solid form. However, it does cost somewhat more than the formula block of about nine parts ethanol and one part A-31 to A-40 which it replaces. It also has a higher evaporative loss rate. Production losses of between 6 to 9% are commonplace, and they get even higher if the methylene chloride is purchased in 600 lb (275 kg) steel drums.

Figure 27. Effect of Methylene Chloride on the Cloud Point of Aerosol Hair Sprays



* This polymer requires less neutralization; it is 9% neutralized with AMP.

Note: Clear points are about 11°F (6°C) higher than cloud points.

During product development, methylene chloride provides the formulator with additional latitudes. An important consideration in hair spray formulations is the cloud point: that temperature below which the resin falls out of solution as a white cloud. Usually it goes back to solution when the temperature is raised to about 10°F (6°C) above the cloud point, but the process may be a slow one. Cloud points below 30°F (-1°C) are generally considered acceptable, those between 30 to 40°F (-1 to 4°C) are somewhat worrisome, and those over 40°F (4°C) are definitely unacceptable, since they will result in consumers encountering clogged valves, erratic sprays and white flecks on their hair in some cases, with practically no holding power. Methylene chloride (and also water) acts to depress substantially the cloud point of resins in ethanol/hydrocarbon and ethanol/CO₂ solutions. Because of this they permit the use of higher percentages of hydrocarbon propellant (a cost saving measure), the use of less compatible resins (such as Resyn* 28-1310 and Luviskol* VA-28), a greater variety of neutralizing agents and (if desired) larger degrees of neutralization than would be otherwise possible. Figure 27 serves to illustrate the effect of methylene chloride as a cloud point suppressant in the case of several hair spray resins.

In a similar fashion Table XLI shows the percentages of methylene chloride, and also water, needed to bring several hair spray formulations down to a cloud point of 0°F (-18°C).

Salon tests have shown that the addition of up to at least 8% water or 16% methylene chloride to hair spray formulas has no negative effect so far as consumers are concerned. This is true even in the so-called "unscented" formulas, where the chemical odor of methylene chloride shows through the very light, nondescript perfumes that are used routinely. On the negative side, the solvent action is sometimes strong enough to loosen hair dyes, dull the plastic frames of eyeglasses, cause skin irritations, and bring about long term degradation of the stem gasket in the aerosol valve, so that the button may tend to stick in the down or actuating position. The solvent has both failed and passed the Ames Mutagenicity (screening) Test, and because of the failure, some salesmen selling brands that are free of methylene chloride will rather unscrupulously show buyers copies of various documents, including one in the *Federal Register*, which cite the Ames test failure and the subsequent concerns of the FDA at that time. This has been a marketing problem to some

TABLE XLI

Effect of Methylene Chloride as a Cloud Point Suppressant in Hydrocarbon Type Hair Sprays

Formulations with cloud points of 0°F (-18°C).

2.0% Resyn* 28-1310 and 0.18% AMP neutralizer:							
Propellant A-40	7.5	10.0	15.0	20.0	25.0	30.0	35.0
Ethanol Concentrate	92.5	84.0	71.0	61.5	51.0	41.0	30.0
Methylene Chloride	0.0	6.0	13.5	18.5	24.0	29.0	35.0
2.0% Resyn* 28-2930 and 0.18% AMP neutralizer:							
Propellant A-40			18.0	20.0	25.0	30.0	35.0
Ethanol Concentrate			82.0	78.5	70.7	62.0	52.5
Methylene Chloride			0.0	1.5	4.3	8.0	12.5
2.0% Gantrez** ES-225, 9% stoichiometrically neutralized with AMP:							
Propellant A-40				20.0	25.0	30.0	35.0
Ethanol Concentrate				80.0	72.0	64.0	54.5
Methylene Chloride				0.0	3.0	6.0	10.5
For Comparison							
2.0% Resyn* 28-1310 and 0.18% AMP neutralizer:							
Propellant A-40	7.5	10.0	15.0	20.0	25.0	30.0	35.0
Ethanol Concentrate	92.5	88.7	81.2	74.6	67.7	insol.	insol.
Water	0.0	1.3	3.8	5.4	7.3	insol.	insol.

*Registered trademark of the National Starch and Chemical Corp.

**Registered trademark of the GAF Corp. 2% solids, or 4% as supplied in 50% ethanol solution form.

extent, for those firms selling hair sprays that contain methylene chloride.

Space does not permit any further in-depth product descriptions of formulas that include methylene chloride, but in summary, this solvent is very important to the industry, its safety has been fully established when it is used under reasonable conditions. It is valuable as a strong solvent, flammability suppressant, pressure depressant and viscosity thinner. The outlook for future growth in aerosol applications suggests a marginally upward trend.

Specialty Gases that Function as Propellents

There are a number of products that contain propellant-type substances where the fact that they are the pressurizing agent is incidental to the central use. Rather common examples include the use of P-12 (CCl_2F_2) in 100% form as refrigerant refills, boat horn energizers, and for fire extinguishers, personal hazard alarm whistles, cocktail glass chillers (now obsolete) and as a dry, inert purging gas in laboratory settings. Similarly, butanes are used as lighter fluids and propane is used as a fuel source for home and industrial paint stripping and welding.

Less routine applications include the use of 100% methyl bromide as a fumigant, particularly for flour and grain products. It is useful for the disinfection and disinsection of commodities on a smaller scale as well. The gas liquid is highly irritating and toxic. It must be handled and filled using extravagant precautions to protect plant personnel. Since it has a boiling point of 38.3°F (3.5°C) and a pressure of 12.9 psig at 70°F (89 kPa at 21.1°C) it is easily handled. The density is 1.732 g/ml at 32°F (0°C). The usual procedure is to strongly refrigerate the material, then pour it into two-piece aerosol cans of a nominal 12-ounce size (actual 368 ml capacity) and crimp the unit with a threaded valve cup. The density allows the can to easily accommodate 1 lb (453.6 g) fills. In order to use the container, a special valve is screwed onto the cap. It carries a needle-like piercing pin that can puncture the cap, and then, upon withdrawal, allow the gas (or liquid, if the can is inverted) to flow out of the can and through a flexible hose connection to the point of use. Since the gas is toxic and also weakly flammable, precautions must be observed during use, similar to those for filling. In the U.S.A. pre-marketing requirements include product registration with the EPA.

The filling of sulfur dioxide [sulfur (IV) oxide; SO_2] into aerosol type cans has taken place in the past but may now be obsolete, at least in the U.S.A. The gas liquid has been used as both a refrigerant and fumigant. It has a boiling point of 14.0°F (-10°C) and a vapor pressure of about 60 psig (250 kPa) at 70°F (21.1°C). It is pungent, poisonous and non-flammable. The usual packaging process is the same as described above for methyl bromide.

The final example of an aerosol dispensed specialty gas is ethylene oxide ($\text{C}_2\text{H}_4\text{O}$). In the pure form it is a very low pressure gas, with a boiling point of 51.3°F (10.7°C). It is extremely irritating and toxic, as well as flammable. The density is 0.887 g/ml at 45.0°F (7°C).

Ethylene oxide is used principally as a gas sterilant, but the sterilizer equipment must be explosion-proof and maintained in special rooms with ventilation, blow-out sections and other precautionary features. A more acceptable procedure is to use a non-flammable mixture of either 12% EtO and 88% P-12, or 10% EtO and 90% CO_2 . The first of these compositions is conveniently blended and packaged into aerosol cans by Benvenue Laboratories (Ohio) and a few other fillers. The usual product consists of a 1 lb (453.6 g) fill in a two-piece aerosol can of 357 ml capacity. The pressure is about 66 psig (455 kPa). These containers may be connected to non explosion-proof sterilizing cabinets in ordinary treatment rooms. In practice, a moderate deep vacuum draw is made on the cabinet enclosure, after which the ethylene oxide mixture is introduced to a pre-set sub-atmospheric pressure. Steam may be pulsed into the chamber during or after the evacuation stage in order to get the relative humidity up to at least 30% and preferably 50% to produce spore hydration so that the EtO cidal activity is accelerated. It also helps warm the chamber to the final sterilizing temperature, which is usually somewhat higher than ambient in order to speed up the first-order sterilizing action. The effects of vacuuming, repressurization and temperature must be carefully evaluated if packaged products are being sterilized, for they could be distorted, lose their sealing integrity and fail in their end-use performance.

The FDA has been concerned about the local and systemic toxic effects of EtO and its reaction products, ethylene chlorohydrin (ETCH) and ethylene glycol (ETG), as well as reports of the mutagenic effects of EtO and ETCH. As a result, in 1978 they established a "Daily Dose Limit" on drugs amounting to 30 g/kg/-

day for 30 days in the case of EtO, as well as an identical level for ETCH and a limit of 1 mg/kg/day for 30 days for ETG. In addition, they will generally defend no EtO sterilization use on foods or cosmetics. On the other hand, cans and bottles can be sterilized, and one firm reliably supplying such a service (for aerosolized

drugs and other products) is the Microbiotrol Division of Griffith Laboratories, Inc. in Alsip, IL.

The aerosol filling of EtO/P-12 products represents only a micro-segment of the aerosol industry, with a volume of only several million units per year. Nevertheless, it stands as an interesting innovation enlarging the scope of beneficial aerosol products into new areas.