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AEROSOL INDUSTRY SUCCESS IN REDUCING CFC PROPELLANT USAGE

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Chlorohydrocarbons	Chlorofluorocarbons	07C
Fluorohydrocarbons		
Packaging		13D
Charging		14G
Dispensers		13I

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Part I - ALTERNATIVE AEROSOL FORMULATIONS

SECTION 1

INTRODUCTION

There is an urgent need to reformulate aerosol products into compositions that no longer contain chlorofluorocarbons ($C_xCl_yF_z$). As early as 1973, scientists recognized that these compounds had very long atmospheric lives and could ultimately penetrate the stratospheric ozone layer at altitudes of between about 14 to 27 km. Once in the stratosphere, CFCs are bombarded with high-energy radiation from the sun, splitting off a chlorine atom that reacts with thousands of ozone molecules and reduces them to ordinary oxygen. Although the ozone is reformed by natural processes over time, the overall effect is of ozone depletion.

During September 1987, a meeting held in Montreal, Canada was attended by representatives of many nations. A treaty known as the Montreal Protocol was developed calling for the orderly reduction of chlorofluorocarbon (CFC) production, roughly according to the following schedule:

By July 1, 1989	Reduction to the 1986 average production level [15-25% actual reduction in the U.S. because of the growth in CFC use since 1986; Ozone Depletion Potential (ODP) basis.]
By July 1, 1993	Reduction to 80% of the 1986 average level, ODP basis.
By July 1, 1998	Reduction to 50% of the 1986 average level, ODP Basis.

As of October 1989, the treaty had been ratified by 43 nations plus the European Community (EC) as a bloc, which together produce approximately 90% of the world tonnage of CFCs.

The results of stratospheric studies made after the Montreal Protocol now strongly suggest that the reduction plan is insufficient to prevent a further depletion of ozone.

Another problem has surfaced, however. As CFCs are phased out, they will be replaced by such chemicals as HCFC-22, 1,1,1-trichloroethane (methyl chloroform) and similar substances, many of which can also deplete stratospheric ozone. Table 1 provides comparative figures.

In 1985, HCFC-22 was responsible for only 0.4% of ozone removal, while 1,1,1-trichloroethane caused about 5.1% ozone removal and CFC-12 was responsible for about 40.1% of the total ozone removal caused by the compounds listed in Table 1. Except for the hydrocarbons and nitrogen, all the compounds in Table 1 are anthropogenically produced.

Such compounds as HCFC-123, HCFC-124, HFC-134a, and HCFC-141b are currently undergoing extensive toxicological testing that is expected to continue until about 1992. HCFC-123 currently has an Acceptable Exposure Limit (AEL), or TLV, of 100 ppm, but this may be changed to somewhere in the 50 to 100 ppm range as further results are developed. Similarly, HCFC-141b may get an AEL of 100 to 300 ppm. Results of the Ames Salmonella Test for HCFC-22, HCFC-141b, and HCFC-142b show positive mutagenic results for all the compounds, but extensive animal testing has clouded the meaning of the Ames results.

TABLE 1. EMISSIONS AND OZONE DEPLETION POTENTIALS OF AEROSOL PROPELLANTS AND RELATED COMPOUNDS

Compound	Structure	1985 Emissions (k tons/year)	Ozone Depletion Potential (ODP) (CFC-11 = 1)[a]
CFC-11	CCl_3F	281	1.00
CFC-12	CCl_2F_2	307	1.0
CFC-113	$CCl_2F-CClF_2$	138	0.8
CFC-114	$CClF_2-CClF_2$	(low)	0.8
CFC-115	$CClF_2-CF_3$	(very low)	0.4 (0.15)[b]
HCFC-22	$CHClF_2$	72	0.05
HCFC-123	$CHCl_2-CF_3$	0	0.02
HCFC-132b	$CH_2Cl-CClF_2$	0	0.05
HCFC-124	$CHClF-CF_3$	0	0.02
HFC-134a	CH_2F-CF_3	0	0
HFC-125	CHF_2-CF_3	0	0
HCFC-141b	CH_3-CCl_2F	0	0.10
HCFC-142b	CH_3-CClF_2	(low)	0.06
HFC-152a	CH_3-CHF_2	0	0
Halon 1211	$CBrClF_2$	3	2.7
Halon 1301	$CBrF_3$	3	10.0
Halon 2402	$CBrF_2-CBrF_2$	(very low)	5.6
Carbon Tetrachloride	CCl_4	66	1.2
1,1,1-Trichloroethane	CH_3-CCl_3	474	0.10 (0.15)[b]
Hydrocarbons	C_3H_3, etc.	(very large)	0
CO_2, N_2O & N_2	CO_2, N_2O, N_2	(very large)	0[c]
Dimethyl ether	CH_3-O-CH_3	42	0

[a]UNEP Data of 18-OCT-1988.

[b]Isaksen, et al (1988).

[c]N_2O can destroy stratospheric ozone but its ODP is undefined.

Many of the future alternative compounds are nonflammable, while others are flammable. HCFC-123 is nonflammable, but a mixture of this gas and 8.8% isobutane is marginally flammable. HCFC-141b has a flammable range of 6.4 to 15.1%, while HCFC-142b's flammable range is 6.7 to 14.9%. HFC-134a, which is being groomed as a replacement for most uses of CFC-12, is nonflammable. HCFC-22 is the only nonflammable (1), commercially available CFC alternative that the industry will have until about 1993 or 1994, when some or all of the second generation CFC alternatives should come onto the market. It is only marginally nonflammable; the addition of 6% isobutane, or 8.6% ethanol to HCFC-22 will produce mixtures of borderline flammability.

The worldwide aerosol business is highly diversified. In 1989, the U.S. will produce about 3 billion units (95% non-CFC aerosols), or 35% of the world total of about 8.6 billion units. Western Europe will produce about 39%, Japan 5%, Brazil 2%, and Mexico 0.5%. Per capita usage is 11 units per person in the U.S.: the typical home contains 46 aerosol products, averaging 206 g per unit. Since the purchase of aerosols is often discretionary (they are not generally considered to be utility products) the per capita usage in different countries is a reflection of both availability and of the relative standard of living. The more hours a person must work to purchase an aerosol, the fewer will be purchased.

Apart from the usual competitive pressures, there is a strong motivation to reduce the costs of aerosol products in order to increase sales. In the U.S., hydrocarbon propellants cost less than 20% of the rapidly escalating costs of CFCs. They are therefore the propellants of choice unless special properties are required, such as better solvent action or reduced flammability. Approximately 81% of U.S. aerosols are pressurized with propane, n-butane, isobutane, or their blends. Another 7% use carbon dioxide, and the remaining 12% use nitrous oxide, CFCs, dimethyl ether, nitrogen, HFC-152a and HCFCs, in approximately that order. The few CFC aerosols remaining after the general ban on these products was imposed during 1978 are those permitted by exclusion, exemption, or those that are not regulated.

Hydrocarbon propellants are already in wide use throughout the world. Examples are as follows: United Kingdom, a market share of 30%; West Germany, 80%; Brazil, 88%; Mexico, 92%; and Canada, 78%. The next preferred CFC alternative is dimethyl ether (DME, or dimethyl oxide). DME alternatives are about 10% more costly than the hydrocarbon alternatives in Western Europe, 100% more expensive in the U.S., and even more costly, or unavailable, in other parts of the world. The major producers are Western Europe, with a capacity of 60,000 tons, Japan, the U.S., Canada, and Australia. Dimethyl ether is flammable. It is also a very strong solvent, sometimes causing gasket failures in equipment, aerosol corrosion, valve seal leakage, and excessive swelling of some elastomers. It is highly water soluble, and can be used as a way of incorporating water into solution in selected aerosol products, such as hair sprays and personal deodorants. Table 2 compares the physical properties of the non-CFC aerosol propellants.

Although carbon dioxide, nitrous oxide, and nitrogen are widely available throughout the world, they have either been ignored or little used as aerosol propellants. These gases are inexpensive, but special equipment is often required to add them to aerosol containers. The simplest of these is the gasser-shaker, of either in-line or rotary construction, which is shaken at a preset frequency and amplitude for a fixed period of time. It is connected through the valve to a supply of gas regulated to a pressure of approximately 142 to 178 psig (10.0 to 12.5 bars). Valve designs are available that will facilitate gas flow into the can, even with the button attached. Since the quantity of gas added will be in the range of 3 to 28 g, depending on can size and content, the weight increase of the dispenser is used as a basis for machine adjustments. Table 3 shows the potential uses of these propellants for several representative products.

HCFC-22 is widely used throughout much of the world as a specialty refrigerant and freezant. Despite its nonflammability (1) and relatively low price (five times more costly than hydrocarbons, in the U.S.), it is not much used. It is limited by its high pressure, which makes it necessary to use 40%

TABLE 2. PHYSICAL PROPERTIES OF NON-CFC AEROSOL PROPELLANTS

Product	Formula	Boiling Point (°C)	Vapor Pressure (bar) 21°C	Vapor Pressure (bar) 55°C	Density at 21° (g/mL)	Flammable Range v.%
nbutane	$n.C_4H_{10}$	-2	1.20	4.79	0.580	1.8 - 8.6
isobutane	$i.C_4H_{10}$	-11	2.17	7.02	0.559	1.8 - 8.5
Propane	C_3H_8	-42	7.60	18.17	0.503	2.2 - 9.5
Dimethyl Ether	$(CH_3)_2O$	-25	4.43	12.40	0.661	3.3 - 18.0
HCFC-22	$CHClF_2$	-41	8.52	20.92	1.208	0
HCFC-142b	CH_3-$CClF_2$	-10	2.04	6.87	1.123	6.7 - 14.9
HFC-152a	CH_3-CHF_2	-25	4.42	12.36	0.911	3.9 - 16.9
Carbon Dioxide	CO_2	-78	58.45	N/A	0.721	0
Nitrous Oxide	N_2O	-88	52.47	N/A	0.718	0
Nitrogen	N_2	-155	N/A	N/A	N/A	0
		FUTURE PROPELLANTS				
HCFC-123	$CHCl_2$-CF_3	28	-0.2	1.7	1.470	0
HCFC-124	$CHClF$-CF_3	-11	3.22	8.8	1.368	0
HFC-125	CHF_2-CF_3	-95	N/A	N/A	N/A	0
HFC-134a	CH_2F-CF_3	-32	5.47	14.3	1.203	0
HCFC-141b	CH_3-CCl_2F	33	-0.3	1.2	1.231	6.4 - 15.1

N/A = Non Applicable, above Critical Temperature.

TABLE 3. PRODUCT APPLICATIONS OF CARBON DIOXIDE, NITROUS OXIDE, AND NITROGEN

Product	Applications
Carbon Dioxide	Hydroalcoholic disinfectant/deodorant sprays.
	Bug killers:
	Ant and roach killers
	Wasp and hornet killers
	Lubricants.
	Anti-statics, soil repellants, and wrinkle removers for textiles.
Nitrous Oxide	Whipped creams.
	Heavy-texture specialty foams.
	Windshield and car lock de-icer sprays.
	Furniture polish.
Nitrogen	Sterile saline solutions for rinsing contact lenses.
	Long-range, stream-type wasp and hornet killers.
	Injector-type engine cleaners.
	Over-pressurant for selected meter-sprayed vitamins and drugs.

or less in formulas and to include suppressive solvents or other propellants to keep the aerosol pressure from being excessive. An interesting blend of HCFC-22/HCFC-142b (40:60) is nonflammable and has a pressure of 63 psig at 70°F (4.43 bar at 21°C). It has been commercialized for perfumes and colognes. HCFC-22 is a good solvent. At less than 28% propellant, its ethanol solutions are lower in pressure than those of CFC-12 and ethanol.

HCFC-142b is used in a few applications in the U.S. and is presently unavailable elsewhere. It is now made by only one supplier, although a second supply source is being developed. As the methyl homolog of HCFC-22, it has many properties in common with the parent compound, except the high pressure. It is more than 12 times as costly as hydrocarbon propellants in the U.S., which has restricted its aerosol applications.

HFC-152a is close to an ideal propellant, except that it is flammable. It is less flammable than hydrocarbon gases, however, and it has typically been used with 70% A-46 (20 mol % propane and 80 mol % isobutane) to produce a propellant for shave creams, depilatories, and mousse products whose foam surface will not momentarily flash if a lighted match is touched to it. The composition is as follows:

60.9% Isobutane
9.1% Propane
30.0% HFC-152a

Since the pressure of the aerosol is about 154 psig at 130°F (11.0 bar at 55°C), according to the partial pressure of remaining air, an extra-strength can is needed.

HFC-152a is noted for its exceptionally low odor and good solvency. It is used to make less flammable colognes and perfumes, especially for those essential oils that might eventually precipitate high-molecular weight resins, fonds, or substantives in the usual ethanol/hydrocarbon (or pure hydrocarbon) systems. Finally, it can be used with many surfactant systems, to partly destabilize aerosol foams, permitting them to be more readily rubbed out on surfaces and not resist liquefaction. A typical product that uses this property is baby oil mousse, which contains 20 to 30% mineral oil.

In the U.S., since HFC-152a is approximately eight times the cost of hydrocarbon propellants, the amounts used in formulas are generally in the 2 to 10% range. It is available in the U.S. and Western Europe, and suppliers claim that distribution systems will be set up to greatly increase world access to this propellant and to HCFC-142b.

The future "CFC alternative" propellants identified in Table 2 are presently undergoing acute, sub-chronic, and chronic (lifetime) toxicological testing. To date, the results have shown some variation in relative toxicity, but indications are that all five compounds will probably be approved for commercial use. The official toxicological reports will be issued in 1992 and 1993, but plans are now in motion to build production facilities well before that time.

In the U.S., DuPont has announced that an existing commercial plant is being converted to produce HCFC-141b and HCFC-142b in 1989. A new plant has been approved to produce large quantities of HFC-134a by 1990. Large quantities of HCFC-123 are already available as a co-product from an existing DuPont facility. And during 1988 DuPont was issued a U.S. Patent on new technology aimed at coproducing HCFC-123 and HCFC-124 in a single process. No schedules for HCFC-124 production have been published.

Other CFC suppliers in the U.S., Western Europe, Japan, and other parts of the world are also studying their options for phasing out CFCs and commercializing various alternatives. The major alternative will probably be HFC-134a, since it will be used to replace CFC-12 in refrigeration, freezant, and air conditioning systems.

An accelerated CFC phase-down program, which goes beyond the Montreal Protocol and is now supported by numerous countries, is based on rapid commercialization and application of the HCFC and HFC alternatives. The science centers around minimizing further increases in the chlorine content of the stratospheric ozone layer.

Table 4 lists the aerosol products currently exempted or excluded from the general regulatory bans in the U.S. on CFCs for aerosol uses. They serve life-saving or other medical purposes, or are considered "essential for other reasons."

A few of these products have been discontinued, such as the drain openers and small-size tobacco barn sprays. The largest users of CFCs are the mold release agents, lubricants, and meter-spray inhalant drug products, except for CFC-12 and CFC-114 small refrigerant recharge units, which many people do not consider to be true aerosol products.

When considering propellants or propellant/solvent combinations that may be used for reformulating CFC aerosols, a large number of attributes must be evaluated. Flammability, toxicology, solvency, cost, availability, solvate formation, solvolytic stability, dispersancy, pressure, and compatibility are some of the more essential characteristics. In the late 1980s, a growing intolerance developed towards propellants and other chemicals that have even slight effects on the stratospheric and tropospheric ecosystems, that have greater perceived toxicity than alternatives, or do not degrade in landfills.

TABLE 4. EXEMPTED, EXCLUDED, OR NONREGULATED CFC AEROSOL PRODUCTS (U.S.)

Mold release agents -- for molds making rubber and plastic items
Lubricants for use on electric or electronic equipment
Lubricants for rotary pill and tablet making presses
Solvent dusters, flushers, degreasers and coatings for electric or electronic equipment
Meter-spray inhalant drugs:
a. Adrenergic bronchodilators
b. Cortico steroids
c. Vaso-constrictors - ergotamine tartrate type
Contraceptive vaginal foams - for human use
Mercaptan (as ethyl thiol) mine warning devices
Intruder audio-alarm system canisters - for house and car uses
Flying insect sprays:
a. For commercial food-handling areas
b. For commercial (international) aircraft - cabin sprays
c. For tobacco barns
d. For military uses
Military aircraft operational and maintenance uses
Diamond grit abrasive uses
For uses relating to national military preparedness
CFC-115 as a puffing (foaming) agent in certain food aerosols
Automobile tire inflators
Polyurethane foam aerosols
Chewing gum removers
Drain openers
Medical chillers - for localized operations
Medical solvents - as a spray bandage remover
Dusters for non electric or electronic uses - for phonograph records and computer tapes
Cleaners for microscope slides and related objects
Foam, whip, or mousse products in general
Small refill units for refrigeration or air-conditioning systems
All other 100% CFC product applications

SECTION 2

FORMULATION GUIDELINES

GENERAL CONSIDERATIONS

Dispersancy, one major attribute of aerosol propellants, is the efficiency with which a propellant can produce a fine spray or an acceptable foam. This is illustrated in Table 5.

The dispersancy of blends can be readily calculated. For example, Propellant A-46 (20 mol% propane and 80 mol% isobutane) has a dispersancy of [549 X .2 + 415 X .8] = 442 mL/g at 21.1°C.

A shave cream or mousse, made using either 8% CFC-12/114, 4% A-46, or 2% nitrous oxide will all show the same properties of foam density and overrun. (However, the nitrous oxide formula will have a very high pressure, which can be expected to decrease significantly with use.)

In the years before the CFC aerosol ban of 1978 in the U.S., hair sprays were commonly formulated with 45% CFC-12/11 (55:45), or 40% Propellant A (10% Isobutane, 45% CFC-12, and 45% CFC-11). They are now formulated with 20 to 26% isobutane, sometimes with a small amount or propane added. These examples show the importance of dispersive effect to propellant volume.

The dispersive effect is not linear but is modified by vapor-pressure, solubility factors, and even by the pressure itself. It normally can be used as a general guideline to determine equivalencies when changing from one propellant choice to another.

TABLE 5. DISPERSANCY CHARACTERISTICS OF VARIOUS PROPELLANTS
(In order of Vapor Volume in mL/g)

Propellant	Vapor Volume (mL/g 21.1°C)	Vapor Volume (mL/mL 21.1°C)
Nitrogen	862	N/A
Carbon Dioxide	549	N/A
Nitrous Oxide	549	N/A
Propane	549	280
Dimethyl Ether	523	345
isobutane	415	234
nbutane	415	239
HFC-152a	365	333
HCFC-22	279	337
CFC-115	256	(not available)
HCFC-142b	240	269
HFC-134a	236	283
HCFC-141b	206	253
CFC-12	200	265
CFC-125	198	227
CFC-11	176	261
HCFC-124	176	242
HCFC-123	158	232
CFC-114	141	207
FC-C318	119	179

Note: These propellants boil at <21.2°C (Range: 23° to 33°C.)
N/A = Not Applicable

The aerosol formulator will also have to determine such things as company policy, availability of equipment, and the safety features of the workplace.

Nonflammable propellants (apart from CFCs) consist of nitrogen, nitrous oxide, carbon dioxide, HCFC-22, and a few blends of other propellants with HCFC-22. Future nonflammable propellants will consist of HCFC-123, HCFC-124, HCFC-125, and HFC-134a. Of these, HFC-134a may become available most quickly worldwide. The cost of HCFC and HFC propellants is expected to be about twenty times that of purified hydrocarbons by 1993 or 1994; this may limit their application to relatively specialized products, for example, to perfume meter-sprays in container sizes of 50 mL or less.

When flammable propellants are considered to be within the scope of company operations, the most reasonable choices are isobutane and propane. In some parts of the world the "natural blend" must be used. A typical natural blend will consist of 60% nbutane, 20% isobutane, and 20% propane. It is a broad distillation cut from the gas wells after de-ethanization and partial de-propanization. In some areas, the hydrocarbon may contain large amounts of other impurities. Some gas wells in Canada were found to contain over 50% hydrogen sulfide and alkyl mercaptans (thiols), causing their closure. Wells in Trinidad typically contain 12% unsaturates, such as propylene and isobutylene, making them marginally useful for aerosol applications. Propane/butanes from gas wells in Brazil contain 2.5 to 5.5% unsaturates.

Any contract filler or self-filler contemplating a change from CFC to hydrocarbon propellants should thoroughly investigate such things as availability, purity, fire and building codes or regulations, the cost of conversion, such as the construction of an outside gas house, safety equipment, and electrical revisions. The product development and quality control laboratories should be equipped with explosion-proof hoods, ventilation, and other safety equipment.

When available, dimethyl ether offers a relatively inexpensive alternative to the hydrocarbon propellants. It does not have the potential problem of odor. It is less flammable (on an absolute, LEL, or other scale) but it is also a very strong solvent.

The flammable HCFCs and HFCs are final options, but because of their relatively high cost they may have a minor effect on the worldwide aerosol industry.

Concentrates

Most concentrates are available in the form of suggested formulations by ingredient suppliers. They may be made especially for aerosol uses, or they may be adaptable to aerosol applications. Some, like most paint products, have to be drastically altered before they will work for aerosols.

A large collection of supplier samples and literature is a requisite of any formulating laboratory. The literature should cover properties, uses, compounding techniques, toxicological data and suggested prototype or starting formulations. (Sometimes these formulas have somewhat more of the supplier's product than is really needed.)

After a concentrate has been tentatively developed, there remains the process of adding the correct type and amount of propellant, and using an aerosol valve that will develop the desired spray pattern or foam puff. One of the most important characteristics that the formulator looks for is particle size distribution, which can be of paramount importance. If the droplet size is too coarse, it can be decreased by one of the following techniques:

- Increase the percentage of propellant;
- Increase propellant pressure and/or dispersancy;
- Use a vapor-tap valve or a larger vapor-tap orifice;
- Use a mechanical break-up button;

- Add a low-boiling (volatile, easy breakup) solvent; and

- Reduce the quantity of polymers, thickeners, resins, adhesives, and water.

Approximately 40-50% of the world's 8 billion aerosol products use vapor-tap valves. Such valves have an orifice extending through the side or bottom wall of the valve body and into the head space area. When the orifice of a vapor-tap valve is enlarged to decrease particle size, a price is paid. The negative effects are listed below:

- A broader particle size distribution will generally result.

- A gradual coarsening of the spray may occur during use.

- The internal pressure will decrease, as air and the more volatile propellant ingredients preferentially escape through the vapor-tap orifice.

- The delivery rate will always be lower than without a vapor-tap, and will decrease during use, because of pressure reduction.

The potential problems with vapor-tap valves can be minimized by the following techniques:

- Use the smallest vapor-tap hole that will suffice (a 0.25 mm size may be a good starting point).

- Use a fairly large to large amount of propellant that disperses well (reservoir effect).

- Use a pure propellant; otherwise, the more volatile ingredient will be preferentially discharged, causing a pressure drop.

- Use reasonably large liquid orifices.

- Emphasize any or all of the above in taller cans, since (near emptiness) a liquid column of 150 - 250 mm will have to be maintained in the dip tube just to bring the product into the valve chamber. A greater dynamic pressure potential is needed, compared with shorter can sizes.

As a rule, thin or driving sprays, or sprays with high delivery rates, will be perceived by consumers as "wet" or "cold," although they may be anhydrous. Wet sprays are usually disliked, except for the coating of inanimate surfaces (such as a paint spray or bug killer); they are most disliked for cosmetic items designed to be sprayed on the skin, such as underarm antiperspirants or deodorants. The aerosol antiperspirant provides an interesting challenge because large valve orifices must be used to prevent possible valve clogging by the 7 to 12% aluminum chlorohydrate powder normally present. Here, the vapor-tap valve, used with a mechanical break-up button, provides a fine-particled spray. The propellant content is in the 68-82% range to give good breakup and to provide an adequate reservoir for the vapor-tap.

Flammability

To devise a good aerosol product, a formulator must try to minimize the risks of flammability and possible explosivity. It is a tribute to the excellence of the aerosol packaging form that extremely flammable products can be safely dispensed, if the user follows the label directions, and if the formulator is able to make allowances for reasonably foreseeable consumer misuse. Flammability is a potential problem when large amounts of product are discharged at one time, as in some hair spray applications, painting, waterproofing, and in the total release insect fogger (TRIF) products. Flammability has also been a problem when containers are dropped on the valve stem, causing it to bend or crack in such a way that the valve jams, releasing a continuous spray. Consumers have sometimes panicked and thrown the can out the window when this happens.

The special case of the TRIF product will be described in more detail later. The latches open on these products, allowing the entire contents of the can, from 50 to 400 g, to be dispensed. Special low-flammability formulas are needed to prevent harmful fireball effects if the spray is discharged too close to pilot lights or other sources of ignition.

In the U.S., aerosol products are regulated according to type by three federal agencies. Pesticides such as insecticides, disinfectants, herbicides, and rodenticides are handled by the U.S. EPA. Household products such as paints, automotive products, air fresheners, and window cleaners, are handled by the Consumer Product Safety Commission (CPSC). Finally, all food, drug, and cosmetic products are under the control of the Food & Drug Administration (FDA). The EPA and CPSC require flammability labeling, according to test method results; the FDA does not. The FDA merely states that products seen to be too hazardous or that are inappropriately labeled will be seized and banned from further marketing. As a result, approximately 70% of all aerosol containers in the U.S. are marked "Flammable." Another 5%, such as many anhydrous automotive products, are marked "Extremely Flammable." Many hair sprays, underarm products, and other FDA-regulated aerosols are also marked "Flammable," although this is not required.

In the U.S. and in most other countries, the standard test method for flammability is the <u>Flame Projection Test</u>. Procedures and criteria vary somewhat, but a can is normally sprayed through the top third of a candle flame from a distance of 151 mm. If the spray ignites and carries the flame forward another 457 mm (or further), the product is considered to be "Flammable." The term "Extremely Flammable" is rarely used in other countries. It relates to two tests, a flashback test and a closed cup flash point test at approximately -28°C. For the product to be marked "Extremely Flammable," it must fail both tests: the flash back must extend to the actuator at any degree of valve opening, and the cup test must indicate a flashpoint of less than -7°C.

Although there are many shortcomings of the Flame Projection Test, which was devised in 1952, it has been adopted by many countries. A number of techniques can be used to reduce the length of the flame in the Flame Projection Test, so that a "Flammable" product can sometimes by "adjusted" to a nonflammable one. For example, hair spray marketers prefer to sell sprays that have flame projections in the 300 to 400 mm range (thus nonflammable). However, these products are marketed with a "Flammable" label that is, in fact, an overspecification.

Methods for reducing flame projection include the following options:

- Reduce the delivery rate;

- Reduce particle size (smaller particles burn out more rapidly and move more slowly);

- Use a vapor-tap button, often with a mechanical breakup button (actually a way to reduce both delivery rate and particle size).

- Add a nonflammable solvent, such as 1,1,1-trichloroethane or methylene chloride, or a nonflammable or less flammable propellant to suppress flammability.

- Present the product as a lotion, foam, mousse, whip, paste, metered dosage (spray or foam, micro or macro) so that the test is passed simply because it cannot be meaningfully applied.

A relatively new concept of flammability arose in 1979 in the U.S. when the Factory Mutual Research Corporation (owned by several insurance carriers) was asked to look into the subject of aerosol hazards in warehouses. Tests showed that many aerosols exploded in fires, producing large fireballs and intense heating effects. Sprinkle systems need to be sized to reflect very high fuel loading.

About 65% of the aerosol cans produced in the U.S. are anhydrous formulations containing flammable solvents and propellants. These require sprinklers capable of spraying from about 3,300 liters/m^2 to 4,200 liters/m^2

(depending on the degree of water miscibility of the flammable ingredients) each minute, for control. Extremely fast response was also a requirement so that the fire could be controlled while still in an early stage.

After a $2 million fire-testing program was finally completed in 1989, the aerosol industry participated in writing new codes and in rewriting others designed to improve the safety features of warehouses, backstock storage areas, and display areas. After a lengthy development protocol, these model codes will be completed and implemented in 1991, after which it is expected they will be adopted by legislative and regulatory officials in local fire and building codes. Since the insurance companies that support the new codes are usually multinational, some effects are already being felt in Europe as well.

Pressure

Most U.S. aerosols are formulated to a pressure as low as is consistent with good operational performance across the anticipated temperature range of their use. For example, hair sprays are expected to work well between 13° - 37°C, and reasonably well just outside these limits.

Pressure limits for containers vary only modestly among countries. In the U.S., the so-called ordinary or non-specification can is permitted to hold product with pressures up to 1,067 kPa abs. (9.85 bar - gauge) at 54.4°C. It will not rupture below 1,546 kPa abs. (14.8 bar - gauge). Special cans with 14% and 28% higher pressure ratings are also available at an extra cost. They only hold about 9% of the market. Aerosols of less than 118 mL capacity are not regulated for pressure limits in the U.S. Most aerosol containers will begin to deform at about 65°C and will rupture at 75°C or higher, depending on can and product.

Materials Compatibility

The formulator's job is not complete when an acceptable product and packaging system has been developed. Test packing is always needed to establish data on weight loss rates, can and valve compatibility, organoleptic stability, etc. Hundreds of sad stories could be written about new products that were inadequately tested, and then could not be manufactured, eroded the can, demulsified, changed color or odor, were subject to microbial proliferation, grew inorganic crystals, or eventually threw down resinous precipitates in the container, swelled valves shut or partly shut, blistered can linings, became latent leakers, etc. No fewer than 36 cans per variable should be test packed and checked--some at about 25°C and some at 40°C; some upright and some inverted.

Tinplate cans do not corrode unless at least 0.008% of free water is present. Above about 0.250%, greater concentrations of water will have no additional effect on the rate of corrosion, if any. Water has little effect on aluminum cans. In fact, its virtual absence can sometimes allow anhydrous alcohol (C_2H_5OH) to attack aluminum cans to produce aluminum ethoxide [$(C_2H_5O)_3Al$] and hydrogen (H_2) gas. Water is implicated in the well-known ability of 1,1,1-trichloroethane to sometimes attack plain and lined aluminum cans, but the mechanism is still unclear. Finally, water can facilitate development of high pH values in hair depilatory formulas and certain others, leading to aluminate (AlO_2^-) ion formation, plus hydrogen (H_2) gas. Since aluminum is amphoteric, it should only be used with formulas having a pH of less than 12.0 at 25°C, and then only when reliably lined.

If a generalized, non-pitting corrosion pattern is seen, it is best to use a lined or double-lined can. Detinning is generally a good sign, showing that the tin (not the iron) is anodic. If pitting is detected, the formula should be changed. Several options are described below:

- Remove the offending or causative ingredient if possible, such as sodium lauryl sulfate, especially if chloride ion is present.

- Add corrosion inhibitors, such as sodium nitrite, sodium benzoate, morpholine, or sodium silicates. (Do not use nitrites in conjunction with primary or secondary amines, or N-nitrosamines will very slowly form in situ. Many of these are carcinogenic.) From 0.05% to 0.20% inhibitor is generally sufficient.

- Increase the pH to about 7.6 to 8.8, if possible, by adding triethanolamine or ammonia (NH_4OH Solution).

- Remove or minimize ionizing materials, i.e., those that permit electroconductivity and thus promote galvanic corrosion reactions.

- Minimize chloride ion (especially). It is a very active corrosion promotor, even for underfilm corrosion. It is critical to minimize chloride ion when materials such as sodium lauryl sulfate (which contains it in some grades) or lauryl polyoxyethylene sulfates are present.

- Sometimes specific corrosion inhibitors are required. Sodium lauryl sarkosinate and sodium coco-B-aminopropionate surfactants are useful for sodium lauryl sulfate. Coco-diethanolamide is good for non-ionic surfactants. Virco-Pet 20 (composition proprietary, except that it is an organic phosphate), is good for dimethyl ether and water compositions.

- For some formulas, traces of moisture can be removed by using such scavengers as propylene oxide or epichlorohydrin. (Very limited evidence suggests that both may be mutagenic.) These chemicals are never recommended for cosmetics.

Many formulations that are intensely corrosive to steel cans may be conveniently packaged in lined aluminum containers. Examples are mousse products and saline solutions. The latter contain 0.9% sodium chloride (NaCl) in water under nitrogen pressure.

SECTION 3

EXAMPLE NON-CFC ALTERNATIVE FORMULATIONS

COSMETICS, TOILETRIES, AND PERSONAL CARE PRODUCTS

Hair Sprays

In the U.S., hair spray (aerosol and pump-action) is the largest single category of the $3,000,000,000 hair care market. Aerosol hair spray is also the largest selling aerosol product. In 1988, about 488,000,000 units were sold, at a retail value of about $1,150,000,000. The pump-spray alternative has several detractions, such as finger fatigue during use, longer application period, flexibility--and sometimes poor shape retention of the larger size containers and occasional plugging of the meterspray valve. The formulations must also be resistant to oxygen, since air is sucked back into the dispenser with every actuation. The pump-action valve is rather costly, and this, combined with a generally smaller fill volume, has necessitated a fairly high price per unit of volume or weight. Sales are relatively small, compared with the popular aerosol version. Both are normally anhydrous and flammable, although there are formulation options for substantially reducing the flammability of the aerosol product.

Hair sprays are normally formulated with 1.3 to 3.0% of film-forming ingredients, commonly called polymers or resins. These materials tack down the hair after the product dries for a minute or two, preventing the displacement of strands or curls by body motion or wind. On the other hand, plasticizers are included to ensure the flexibility of the entire hair mass, so that it can retain a healthy bounce and not feel too stiff. A feature of some formulas is that extra stiffness can be imparted by spraying on more product, if a more sculptured or rigid coiffure is desired.

The hair spray resin must have properties that include solubility in 95.5 vol% of anhydrous ethanol, a good feel on the hair, no stickiness or tackiness in moist atmospheres, lustrous (healthy) appearance, good holding power, good removability with shampoos, and sufficient flexibility to allow bounce and to resist junctural fracture.

To achieve the ideal property mix, nearly all film-forming resins are copolymers (dipolymers and terpolymers). Of the seven or so used in the U.S., perhaps the most popular is Gantrex ES-225, made by the GAF Corporation. Chemically, it is the monoethyl ester of polyvinylmaleate/maleic anhydride copolymer, and it is normally purchased as a viscous solution of 50% solids in anhydrous ethanol. For best results, the carboxylic acid moieties of the polymer must be partially neutralized by the addition of certain amine compounds. Another polymer, known as Gaffix, was introduced by the same supplier in 1989 and is said to provide not only hair fixative properties but hair conditioning as well. (The same quaternized material is recommended for hair mousses.)

The type and amount of resin and plasticizer (if needed) enables the final product to be sold as a Gentle Hold, Regular Hold, Extra Hold, Super Hold, or Ultimate Hold formulation. The differences between such products vary: a Regular Hold by one marketer may have more holding power than an Extra Hold by another. In popularity, the Extra Hold and its equivalents have a slight advantage, closely followed by the Regular. While hair sprays normally fall between the "price/value" (utility) and "luxury image" ends of the hair care market, many sell for several times the price of others. The "luxury image" products do not usually indicate their hair-holding ability, preferring to suggest that they are just right for all users.

During the 1970s, many hair sprays were extended to provide supplementary benefits by the inclusion of such minor ingredients as Vitamin E (alpha tocopherol), silicones, myristyl myristate, aloe extract, elastin, and protein hydrazolates. The products of the 1980s still use many of these special ingredients, but also claim to be "energizing," "volumizing," "revitalizing," "nourishing," "elasticizing," and good for "sun survival." Since hair is dead matter, some of the claims refer to the scalp, not to the hair shaft.

The formulas in Table 6 illustrate ways of using both hydrocarbons and dimethyl ether as propellants.

The use of water with Gantrez and Resyn copolymers in hydrocarbon-propelled hair spray systems has been the subject of U.S. Patents held by the American Cyanamid Company. Patents have also been issued covering the inclusion of carbon dioxide as an additional propellant in dimethyl ether systems. Both carbon dioxide and nitrous oxide are extraordinarily soluble in dimethyl ether, dissolving at about 3.70% and 3.91%, respectively, for each one bar of pressure increase at 21°C.

In the U.S., the hydrocarbon hair sprays have generally been packed in lined tinplate or (sometimes) aluminum cans. In other countries, plain tinplate cans are often used. The dimethyl ether formulas are usually packed in plain tinplate cans or in aluminum cans with linings of PAM (polyamidimide) or special epon-phenolic types.

The Precision Valve Corporation has developed effective valves for both hydrocarbon- and dimethyl ether-based hair sprays, using their well-known 2 X 0.50 mm Aquasol® stem. Other components include a 0.50 mm MBST (Mechanical Break-up Straight Taper) button and butyl rubber stem gasket. The very high solvency effects of dimethyl ether require special gaskets for valves. For valve cups, cut gaskets of Butyl U105, Butyl U133, and Chlorobutyl CLB-82 (all by the American Gasket and Rubber Company) have performed well commercially. The Precision Valve Corporation's Polyethylene-Sleeve gasket also gives good performance when used with tinplate cans, as do the polyethylene and ppolypropylene laminates.

Since the drying time of alcohol is 29 times as quick as that of water, it may be surprising to know that the drying time of all four hair spray formulas is essentially the same. This is because the formation of

TABLE 6. HAIR SPRAY FORMULATIONS USING BOTH HYDROCARBON AND DIMETHYL ETHER PROPELLANTS (Regular Hold)

Ingredients	Formula A	Formula B	Formula C[a]	Formula D[a]
Gantrex ES-225 (50% in Anhydrous ethanol)	4.00	4.00	----	----
Resyn 28-2930 (100%)[b]	----	----	2.50	2.50
Amino-methyl-propanol (95%)	----	0.09	0.20	0.18
N,N-Dimethyl-octadecylamine	0.29	----	----	----
Dimethyl Phthalate	0.03	----	0.03	----
D.C. Fluid #193[c]	0.02	0.02	0.04	0.06
Disodium Dodecylsulfosuccinate	----	----	0.20	0.20
Sodium Benzoate	----	----	0.08	0.08
Fragrance	0.10	0.10	0.15	0.15
Deionized Water	----	8.79	16.00	32.00
S.D. Alcohol 40-2 (Anhydrous)	67.56	61.00	44.80	28.83
Propellant A-31 or A-40[d]	28.00	26.00	----	----
Dimethyl Ether	----	----	36.00	36.00
Pressure (532 mm Vacuum Crimp, 21°C)	2.2 bar	2.5 bar	2.5 bar	3.7 bar
Delivery Rate (g/sec - 21°C)	0.50	0.54	0.60	0.65
Flame Projection (mm - 21°C)	460	425	250	225
Flash Back to Button[e] (mm - 21°C)	60	50	0	0

[a]Formulas C and D are based on information originally developed and published by Dr. Leonidus T. Bohnenn of Aerofako, BV.

[b]Vinylacetate/crotonic acid/vinyl neodecanoate copolymer, made by National Starch & Chemicals Corporation, U.S. (It can be replaced with Gantrez ES-225, but some detinning may occur at 35°C or above.)

[c]A water-soluble silicone copolymer, made by the Dow-Corning Corporation, U.S.

[d]A-40 is an alternative propellant blend, consisting of 10% propane and 90% isobutane by weight. The pressures and other data for Formulas A and B are based on A-31; 100% isobutane.

[e]At full delivery rate. If the valve is throttled, the flashback of Formulas A and B will become 152 mm; i.e., to and touching the actuator.

hydroalcoholic dimethyl ether azeotropes greatly accelerates the evaporation rate of water. (This feature is useful in dimethyl ether formulations for personal deodorants, paints, and several other aerosol products.)

Until recently, methylene chloride, and, rarely, 1,1,1-trichloroethane were included in U.S. hydrocarbon hair sprays. These solvents were removed in between 1985 and 1988 because of the alleged carcinogenicity of these substances.

Since the early 1950s, methylene chloride has been used in billions of cans of hair sprays. It increases resin solvency, decreases flammability, promotes evaporation rate, and causes the deposition of a smoother film with less junctural beading. Concentrations of up to 25% have been tolerated by both the dispenser and the consumer. In greater amounts, however, the odor and solvent effects become more significant. For instance, plastic eyeglass frames may glaze over time, and contact lenses may blush temporarily. A few individuals are sensitive to methylene chloride and may develop rashes or itching of the neck.

Hair Lusterizers

Many people, but especially those Blacks, Hispanics, and others with very curly hair, have little need for standard hair sprays, but they often use hair conditioning and lusterizing sprays that convey the sheen and look of naturally healthy hair. Some formulations for these products appear in Table 7.

Both hair sprays and hair lusterizers are sold in scented and unscented versions. The "unscented" form actually has about 0.02 to 0.03% of a nondescript floral fragrance in it to cover the slight chemical odors of the other ingredients. They are also sold for both consumer and professional end uses. The professional cans are often quite large [65 mm X 238 mm (666 mL fill)], and are generally of tinplate.

TABLE 7. HAIR CONDITIONER SPRAY FORMULATIONS

Ingredients	Formula A	Formula B	Formula C	Formula D
Isopropyl Myristate[a]	----	----	2.0	2.0
Mineral Oil; USP	----	3.0	----	----
Isodecyl Oleate	5.0	----	----	----
Volatile Silicone Fluid[b]	----	20.0	----	----
Odorless Mineral Spirits	35.0	----	20.0	20.0
PPG-12/PPG-50 Lanolins	----	----	3.0	3.0
Pluriol 9400[c]	----	----	----	0.03
Mink Oil	0.1	0.1	0.1	0.07
Fragrance	0.1	0.1	0.1	0.1
Deionized Water	----	----	----	15.0
S.D. Alcohol 40-2 Anhydrous[d]	19.8	----	44.8	24.8
Iso-Butane (A-31)	----	76.8	30.0	----
Propane/iso-butane (A-46)	40.0	----	----	----
Dimethyl Ether	----	----	----	35.0
Pressure (532 mm Vacuum Crimp) (bars, at 21°C)	3.6	2.6	2.4	2.9

[a]Cosmetic Grade. May be replaced by isopropyl palmitate.

[b]As Cyclomethicone F-251 (Dow-Corning Corporation). A blend of 25% Tetrameric Ring Compound and 75% Pentameric Ring Compound. The dimethylsilicone of 0.65 cstks. Viscosity may also be used.

[c]A propylene oxide - ethylene oxide surfactant polymer.

[d]Specially Denatured ethanol. To make, add 400 g t.Butanol and 45 g of Brucine Sulfate to 3,784 liters of ethanol.

Hair Mousse

The mousse (French word for "foam") was first introduced in an aluminum can in the U.S. in 1973 as "Balsam and Body" foam. The French-based firm of L'Oreal, S.A., which researched this product type from 1975 to 1980, required a hair setting and conditioning foam that would leave the hair softer, more manageable, easier to brush, shiny, free of frazzles, having a good handle and slip, and with good body control and able to resist fly-away situations. The product was launched in Europe in 1981 and in the U.S. and Japan in 1983. In 1988, world-wide sales were about 270,000,000 aluminum cans; about half of this number was marketed in Europe.

To achieve both hair set and conditioning characteristics, any one of three classifications of a specialty polymer must be used:

- A combination of a slightly anionic "hair spray" film former, with a compatible cationic hair conditioning polymer;

- A cationic conditioning polymer that can also function as a hair-setting agent; or

- An amphoteric hair-setting and conditioning polymer, sometimes augmented by the addition of quaternary conditioning ingredients.

One of the more popular compounds is Gafquat 755N (20% dispersion in water), which is a quaternary ammonium polymer formed from dimethyl sulfate and a copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate. The second approach is to use a two-component system, such as a combination of GAF Corporation's Copolymer 845 (20% in water) poly(vinylpyrrolidone/dimethyl-aminoethyl methacrylate, for hair setting plus a quaternary, such as Ciba-Geigy's Bina Quat 44C: hydroxyl-cetylammonium phosphate. Supporters of the two-component system claim they can adjust the degree of set and degree of conditioning independently, to conform to perceived marketing requirements. A large number of other products are available, but the anionic and cationic moieties have to be selected for compatibility or precipitation may occur. A well-quaternized resin will exhaust substantively onto the towel-dried hair when the product is worked into it following shampooing. In a typical case, about 175 mg per 100 g of hair will exhaust from dispersions of 0.3% concentrations or higher in the product itself. This 0.175% level is all at the hair surface, and provides such properties as silkiness, shine, volume, handle, lack of fly-away, lubricity, manageability, and anti-static properties. It also avoids any sense of limpness or buildup on the treated hair.

After the hair set and conditioning agents are chosen, an emulsifier must be selected. A minimum amount should be employed, so the user can apply the mousse without needing to rinse the excess out of the treated hair. This is especially important in the case of emulsifiers, where the excess can turn the hair slightly waxy, sticky, and dull. Some common selections include oleyl diethanolamide, ethoxylated (9 mol) octylphenol, polyethylene glycol (10 mol) ether of stearyl alcohol, mixed monooleate esters of sorbitol and sorbitan anhydride with an average of 20 moles of added ethylene oxide (Polysorbate 80) and polyethylene glycol (20 mol) ether of stearyl alcohol (Brij 720 or PEG-20 Stearate). In general, the most effective are nonionic ones at levels of 0.3 to 0.7%. The emulsifier must ensure good dispersion of the propellant, good foam formation, and some initial instability of the foam when applied. It must quickly collapse when rubbed onto the wet hair. Good wet and dry combing, foam wetting, moisture retention, and emmolliency are generally conveyed by the use of these ethoxylates and propoxylates.

Like the hair sprays and lusterizers, mousse products often contain a host of specialty ingredients at levels often ranging from 0.001 to 0.100%. These include aloe vera extract, jojoba oil, chamomile extract, protein derivatives, elastin, allantoin, other quaternaries, birch (tree) extract, marigold (flower) extract, walnut leaves (tree) extract, and various sunscreening agents. They may or may not convey any real benefit, depending on the concentration used in the formula. Some mousse products also contain colorants or dyes, of which perhaps the most common is FD&C Yellow #7 (in the U.S.), used at 0.002 to 0.008%. All mousses are perfumed.

Bacterial proliferation can occur in some mousse formulas, so they are often protected with 0.10% methyl p.hydroxybenzoate and 0.05% n.propyl p.hydroxybenzoate. Other, more powerful and broader spectrum preservatives are now being favored, such as Kathon CG (Rohm & Haas Company) and Dowicil 200 (Dow Chemical Company). In general, the finished mousse concentrate or aerosol should be able to pass a microbial Total Plate Count test with a reading of "less than 10 organisms per mL." It is also recommended that the tank, hoses, pumps, filters, and filler bowls be sanitized and that the deionized water used in batchmaking be first heated to 70°C to kill pseudomonads and most other microorganisms.

The usual propellant for mousse products ia A-46 (15 weight % propane, in 85 weight % isobutane), which develops mousse pressures in the area of 4.0 bar at 21.2°C. The usual amount is 6.5 to 7.5%, but some products use as much as 15%. For some specialty products, such as mousse used on babies, absolutely no evidence of flammability can be tolerated. With the straight hydrocarbon formulas, touching a lit match or lighter to the surface of the foam will produce a momentary ignition. This can be eliminated by using a propellant blend that includes 30% or more HFC-152a. The A-46 and HFC-152a can be purchased as a blend, premixed by those fillers who have blending stations, or added consecutively using two separate gassing machines. Because the HFC-152a is only present in concentrations of 2% or so, the cost penalty is relatively low.

The general considerations involved in formulating a mousse hair set and conditioning product have been described, and some illustrative formulations will now be presented. Table 8 describes four formulations fully, giving first the U.S. Cosmetic Ingredients Dictionary (CTFA-CID) terminology, followed by the chemical name, brandname(s), and source. Table 9 describes four additional formulations in a format of decreasing order of ingredient concentration (except that ingredients whose concentrations are less than 1% may be placed in any order), in accordance with U.S. Food and Drug Administration (FDA) regulations. These regulations require ingredients of food, drugs,

TABLE 8. MOUSSE HAIR SET AND CONDITIONING PRODUCT FORMULATIONS

Formula A	% (w/w)	
	Soft Set	Firm Set
Polyquaternium 4 Copolymer of hydroxy-methylcellulose and diallyl-dimethyl ammonium chloride Celquat L-200 (100% A.I.) by National Starch & Chemical Corporation	0.60	1.00
Deionized Water	75.85	75.25
Dimethacone Dimethyl silicone derivative emulsion DC Silicone Emulsion by Dow-Corning Corp.	0.15	0.20
Tallow Trimonium chloride (and) isopropanol stearyl/palmityl trimethyl ammonium chlorides; 75%, in isopropanol Arquad T-50 (75% Active Ingredient) by the Industrial Chemicals Division of Armak Corp.	0.10	0.15
Octoxynol 9 Ethoxylated (9) n.Octylphenol Triton X-100, by the Rohm & Haas Corp.	0.15	0.30
Emulsifying Wax NF Fatty alcohol derivative - Self emulsifying Polawax A-310, by Croda, Inc. Polawax A-310, (100% A.I.) by Croda, Inc.	0.15	0.10
Ethanol SD40 Ethanol (Denatured #40; 100%) S.D. Alcohol 40; anhydrous, by U.S. Industrial Chemicals Division	14.90	14.88
Perfume Oil (Floral)	0.10	0.12

Continued

TABLE 8. (Continued)

Formula A		
Ingredients	**% (w/w)**	
Propellant A-46 15 wt. % propane & 85 wt.% isobutane A-46 Propellant by Phillips Petroleum Co.; Specialty Products Division	8.00	8.00

Formula B	
Ingredients	**% (w/w)**
Quaternium 11 Poly (vinylpyrrolidone/dimethylaminoethyl methacrylate) Copolymer 845 (20% Solids in Water) by GAF Corp.	7.00
Polyquaternium 16 Hydroxyethyl cetyldimonium phosphate (100% A.I.) Bina-Quat 44C (100% A.I.) by Ciba-Geigy Corp.	3.50
Cocoamid DEA Coconut acids diethanolamine condensate (1:1) (Free of soap and amide esters) (Superamide) Standamid SD (100% A.I.) (Henkel Chemical Co.)	1.00
Tallow Alkomium Chloride Dimethyl benzyl tallow ammonium chloride Incroquat S85 or SDQ-25 (Croda, Inc.)	0.50
Deionized Water	77.65
Methylparaben Methyl p.hydroxybenzoate Nipagin M (Nipa Laboratories, Ltd.)	0.08
Perfume Oil (Floral)	0.26
FD&C or D&C (Color)	0.01
Propellant A-46 16 wt % propane & 84 wt % isobutane A-46 Propellant by Phillips Petroleum Co.; Specialty Products Division	10.00

Continued

TABLE 8. (Continued)

Formula C	
Ingredients	% (w/w)
Polyquaternium 11 A quaternary ammonium polymer formed by the action of dimethyl sulfate on a copolymer of vinylpyrrolidone and dimethyl amino ethyl methacrylate. Gafquat 734, (50% A.I. in Ethanol), by the GAF Corp.	1.32
Polyquaterium 4 A copolymer of hydroxymethylcellulose and diallyl-dimethyl ammonium chloride. Celquat H60 (100% A.I.) by National Starch and Chemical Corp.	1.00
Silicone Silicone polymer, end-blocked with aminofunctional groups Cationic Emulsion 929 Dow-Corning Corporation	0.15
Oleamidpropyl Dimethylamine Hydrolysed Animal Protein Oleylamidopropyl diethylamine hydrolysed animal protein. Lexein CP-125, by the Inolex Corp.	0.20
Potassium Coco-hydrolysed Animal Protein Animal protein hydrolysed in boiling potassium cocoate soap solution. Lexein S620, by the Inolex Corp.	0.14
Aloe vera Aloe vera Aloe Vera: Pure Extract (90% A.I. Powder), Terry Chemical Company	0.05
PEG 150 Hydro-(ethyleneoxide 150) alcohol Carbowax 8000, by Union Carbide Corp. or Polyethylene Glycol 6000 by Dow Chemical Company	0.26
Quatermium 52 Dibutyl sebacate Dehyquart SP, by Henkel Chemical Company	0.20

Continued

TABLE 8. (Continued)

Formula C	
Ingredients	**% (w/w)**
Ethanol SD40 Ethanol (specially denatured #40; 100%) S.D. Alcohol 40; Anhydrous, by Shell Chemical Co.	3.00
Polysorbate 20 Mainly the monolaurate ester of sorbitol and sorbitol anhydrides, condensed with 20 moles of ethylene oxide. Tween 20 by ICI Americas, Inc., or Nikkol TL10 or TL10-EX by the Nikko Chemical Company	0.05
Fragrance (Floral)	0.209
FD&C or D&C (Color)	0.001
Deionized Water	85.42
Propellant BIP-55 Ethane 0.290 w.% Propane 30.728 Iso-butane 26.509 n.Butane 39.759 Pentanes 2.700 Hexanes 0.010 Unsaturated Hydrocarbons 0.001 maximum Sulfur compounds 0.0005 maximum Water 0.0025 maximum Propellant IBP-55 by Phillips Petroleum Company, Specialty Products Division.	8.00

Formula D	
Ingredients	**% (w/w)**
Polyquaternium 11 Quaternary ammonium polymer of dimethyl sulfate and the copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate. Qafquat 755N (20% in water), by GAF Corp.	5.00

Continued

TABLE 8. (Continued)

Formula D	
Ingredients	% (w/w)
PVP Polyvinylpyrrolidone (Mol. wt. = 30,000) PVP (K-30) (GAF Corp.)	1.00
Carbomer 941 Polymer of acrylic acid, cross-linked with a polyfunctional agent Carbopol 941 (Use as 2.0% in Water) B.F. Goodrich & Co.	15.00
Ammonia Ammonium Hydroxide (29% in Water)	0.28
Steardimonium Hydrolysed Animal Protein - Purified. Stearyl dimethyl ammonium modified hydrolysed protein Croquat SP (Croda, Inc.)	0.28
Nonoxynol-20 Ethoxylated (20) n.nonylphenol Igepal CO-850 (GAF Corp)	0.28
Steareth-2 Polyethylene glycol (2) ether of stearyl alcohol $CH_3(CH_2)_{16}CH_2(OCH_2CH_2)_2OH$ Brij 72 (ICI Americas, Inc.)	0.28
Polysorbate 20 Mainly the monolaurate ester of sorbitol and sorbitol anhydride, condensed with an average of 20 moles of ethylene oxide. Nikkol TL10 or TL10-EX (Nikko Chemical Co.)	0.50
Methylchloroisolthiazolinone and Methylisothiazolinone Iathon CG (Rohm & Haas Company)	
Fragrance	0.24
Deionized Water	68.00

Continued

TABLE 8. (Continued)

Formula D	
Ingredients	% (w/w)
Hydrofluorocarbon 152A 1,1-Difluorethane	6.40
Dymel-152 (E.I. DuPont de Nemours & Co., Inc.) Genetron-152a (Allied-Signal Corporation)	
Isobutane Isobutane A-31 (Phillips Petroleum Co.) Aeron A-31 (Diversified Chemicals and Propellants Co.)	2.74

TABLE 9. INGREDIENT LISTINGS OF OTHER MOUSSE HAIR SETS AND CONDITIONERS[a]

1. XYZ Co. Professional Designer Mousse

So Airy-light	Extra Firm	Alcohol Free	With Sunscreen

Water
Hydrofluorocarbon 152A
Isobutane
*Polyquaternium-11
*DEA-Methoxycinnamate
Polyquaternium-4
Dimethacone Copolyol
Fragrance
*Isosteareth-10
Sodium Cocoyl Isethionate
Methyl Paraben
*Lauramide DEA
*DMDM Hydantoin

2. DO-GLO XYZ Co. Alcohol-Free Styling Mousses

A 230-gram fill in aluminum can

Ultimate Hold - for all Hair

Water
Isobutane
PVP/Dimethylaminoethyl methacrylate copolymer
Polyquatermium 4
*Diphenyl-dimethicone
*Lauramine Oxide
DMDM Hydantoin
Fragrance
*Quaternium 18
Butane
*Ammonium Laureth Sulfate
*Disodium Ethylenediamine Tetraacetate (EDTA)
Citric Acid

Continued

TABLE 9. (Continued)

3. DO-GLO XYZ Co. Alcohol-Free Styling Mousses	
	A 230-gram fill in aluminum can
	Extra Body - for Fine Hair
	Water Isobutane Polyquatermium 4 Propane *Lauramine Oxide Propylene Glycol *Octyl Salicylate Panthenol *Silk Amino acids *Keratin Amino acids *Hydrolysed Animal Keratin Butane Citric Acid DMDM Hydantoin Fragrance *Disodium Ethylenediamine Tetraacetate (EDTA)
4. DO-GLO XYZ Co. Alcohol-Free Styling Mousses	
	A 230-gram fill in aluminum can
	Moisture Rich - for Dry or Damaged Hair
	Water Propane Isobutane *Acetamide Monoethylamide (MEA) PVP/Dimethylaminoethylmethacrylate Copolymer Butane Cocamide Diethanolamide (Superamide) Panthenol (N-Pantothenylamindoethyl) disulfide *Glycereth-26 *PEG-150 Distearate Sodium Lactate *Sodium PCA Collagen

TABLE 9. (Continued)

[a]All ingredients are listed in decreasing percentages, except for those present in concentrations of less than 1.0 percent.

*These ingredient designations are identified chemically in the following way:

Acetamide MEA: Acetamide Monoethylamide Lipamide MEAA (Lipo Chemicals, Inc.)

Ammonium Laureth Sulfate: Ammonium salt of ethoxylated (1-4) lauryl Sulfate Carsonol ALES-4 (Lonza Chemical Corp.)

DEA-Methoxycinnamate: Diethylaminomethoxycinnamate (Sun Screen Agent)

Diphenyl-trimethicone: Silicone 556 Fluid (Dow-Corning Corporation)

Disodium EDTA: Disodium Ethylenediaminetetraacetate

DMDM Hydantoin: 1,3-Dimethylol-5,5-Dimethyl Hydratoin

Glycereth-26: Polyethylene Glycol (26) Glyceryl Ether Ethosperse G-26 (Glyco Chemical Company)

Hydrolysed Animal Keratin: Keratin, hydrolysed

Isostreareth-10: Polyethylene Glycol (10) Ether of Isostearyl Alcohol

Keratin: Keratin Amino Acids Kerapro (Hormel Company)

Lauramide DEA: Lauric Acid - Di-ethanolamide (1:1) Condensate Super-amide

Lauramine Oxide: n.Lauryl-dimethylamine oxide

Octyl Salicylate: 2-Ethylhexyl Salicylate $C_{15}H_{22}O_3$ (Sunarome WMO-Felton)

PEG-150 Distearate: Polyethylene Glycol (150 mol) Distearate Lipopeg 6000-DS (Lipo Chemicals, Inc.)

Polyquaternium 11: A quaternary ammonium polymer formed from dimethyl sulfate and a copolymer of vinylpyrrolidone and dimethyl amino ethyl methacrylate.

Quaternium 18: De(hydrogenated tallow) Dimethylammonium Chloride Adogen 442 (Sherex Corporation)

Silk Amino Acids: Amino Acid Blend, derived from Silk Protein (Croda, Inc.)

Sodium PCA: Nalidone (UCIB) U.S. Distributor: S.S.T. Corporation (Clifton, NJ) and cosmetics to be listed on the product label in this fashion, unless they are for professional or institutional use.

Containers for Hair Setting and Conditioning Mousses.

Mousse formulas are normally finished to a pH value of approximately 5.5 to 6.5 at 25°C. They are either aqueous or hydroalcoholic and contain surfactant wetting agents and a high concentration of chloride ion, a well-known corrosion promoting agent. It is not surprising that they are corrosive to steel and tinplated cans and may even attack aluminum cans unless they are well lined. Many mousse formulations contain corrosion inhibitors, such as sodium benzoate, coco-diethanolamide, and amino groups to provide additional shelf-life stability.

During 1984 and 1985, a large amount of work went into developing well-lined tinplate cans for mousse formulas to take advantage of the much lower prices of tinplate. In 1984, one major marketer introduced a low-priced mousse in a 45-mm diameter tinplate (necked-in) can. Special techniques were used to make the formula less aggressive, and the can was heavily double-lined with an Organosol hydridized vinyl coating system. The product is still doing well on the market. The only other mousse products in tinplate cans are lines of large, salon-type mousse products sold to a number of marketers by one formulating house. The cans are 52 mm in diameter by approximately 190 mm in length. They have necked-in construction. They are made only by the Continental Can Unit of the United States Can Company and, uniquely, use a third body lining (after welding and flanging) as a repair coat, to cover up any abrasions or scratches made during manufacture. These cans contain 298 g of product. A developmental can of polypropylene-laminated tinplate or tin-free steel is performing well with mousse products after a year of storage.

Aluminum cans for mousse applications are typically 38, 45, or 52 mm in diameter and are up to 165 mm long. All are of one-piece construction and are heavily single or double lined. The usual epon-phenolic linings for aluminum cans are sometimes inadequate for mousse products and have generally been replaced with linings made of pigmented epoxy-phenolics, PAM clear polyamidimide, and the popular Micoflex L6X392 beige-pigmented vinyl Organosol. In some cases, two separate linings of the same material are applied.

Nearly all valves for mousse hair care products use aluminum mounting cups coated on the outside and lined on the inside surfaces. Numerous problems have arisen from trying to make a good seal, especially in the case of the larger-diameter 52- and 66-mm cans. Bonded polyethylene sleeve gaskets (an exclusive development of the Precision Valve Corporation) are satisfactory if the new Ring Seal mounting cup contour is used, as are the full-coverage polyethylene laminate gaskets--again, if a special contour valve cup is used. These gaskets require a special mousse-resistant adhesive if continuing attachment to the inner surface of the valve cup is a marketer requirement. Otherwise, the laminate will separate eventually and droop slightly. Some technical experts are concerned about the possible corrosivity of concentration cells that can be created between the laminate and unprotected aluminum cup. Any liquids that may accumulate there must enter by permeating the polyethylene; therefore, unknown compositions and concentrations may form. Also, the adhesive is generally an excellent barrier material, but this advantage is lost if delamination occurs.

Most hair care mousse products are designed to be vertical acting. Full coverage of the mounting cup is an aesthetic benefit. The "pad-and-smokestack" type is popular, as is the tilt-action, simple "smokestack" design. Foam spouts are either white or the color of the base coat of the can. The protective cover will either fit over the spout or valve cup outside diameter, or be designed to have the same diameter as the can, for a cylindrical look.

Many U.S. marketers are testing the Fibrenyle Ltd. "Petasol" or PET (polyethylene terephthalate) plastic bottles for mousse applications, with good results. One problem that must be resolved is that the U.S. Department of Transportation (DOT) will not permit interstate shipments of non-metallic aerosol containers if their capacity exceeds 118.3 mL because of a regulation that dates back to 1951, when the only non-metallic aerosol containers were those made of glass. Special exemptions based on impressive arrays of test data, including drop test results, have now been requested. Meanwhile, several new bottle shapes are being developed.

Other Mousse Products

The original hair setting and conditioning mousse products of 1981 and later have made it possible for marketers to successfully introduce an impressive number of related foam products. Several still involve various aspects of hair care, such as hair sheens or lusterizers, hair depilatories, dandruff control foams (using zinc pyrithrone or an alternative dandricide), hair coloring mousses, and mousse products to help control ear itch and "jock itch," a trichophytal fungal mycosis of the pubic area related to the well-known "Athlete's Foot" problem. Other hair care products include baby oil formulas, baby shampoos, curl activators, and products that promise a hair thickening effect. A hair restorative material is now being sold in mousse form.

The remaining second-generation mousse products are generally for skin care. They include make-up items, baby oil formulas (again), sunscreens, facial cleansing foams, hand creams, skin smoothing (20% talc) products, cationic skin emollients, dewrinkler formulas, etc. Mousse products can be used to contain and deposit large amounts of specialty oils on the skin, such as a product that contains 25% jojoba oil (Wickenol 139, Dow-Corning Corp.), which claims to give the skin a healthy sheen and superior lubricity.

The specialty "mousse gels" consist of lines of products that deliver as clear or translucent gels but spring into mousse foams on contact with the hand. Table 10 presents several formulations illustrating these newer products.

The mousse packaging system is an ideal vehicle for dispensing sunscreens and suntan lotions as foams that quickly break up on mechanical shearing to produce exceptionally even matte finish results. The first to introduce this product was Schering-Plough, Inc. as one of several package forms for Coppertone. More recently, in 1984, the Golden Sun Company introduced their Sun Goddess Body Mousse Protective Sun Tan products in a 170-g filling weight.

TABLE 10. SPECIALTY MOUSSE FORMULATIONS

Formula E

Hair Sheen and Conditioner

Ingredients	% (w/w)
Stearimidopropyl Cetaryl Cimonium Tosylate (and) Propylene Glycol. (Ceraphyl 85, by Van Dyk & Co., Inc.)	0.50
Quaternium 26 (Ceraphyl 65, by Van Dyk & Co., Inc.)	0.75
C9-11 Isoparaffins (99+% C_9-C_{11} Branched Paraffinics) Isopar K, by Exxon, Inc.	20.00
Isodecyl Oleate	4.00
C12-15 Alcohols Benzoate	1.00
Fragrance	0.25
Deionized Water	68.50
Isobutane A-31 (Aeropres Corp.) (Propellant A-46)	4.25
Propane A-108 (Aeropres Corp.) (Propellant A-46)	0.75

Note: The foam may be destabilized by adding 0.5% of a volatile silicone such as CTFA Cyclomethicone, alcohol, or by replacing part or all of the hydrocarbon propellant (A-46) with hydrofluorocarbon 152 (CH_3 - CHF_2). Stability can be increased by adding cetyl alcohol.

Formula F

Baby Shampoo and Conditioner

Ingredients	% (w/w)
Sodium Laureth (3) Sulfate [Sodium Lauryl (3 ETO) Sulfate]	40.00
Cocoamidopropyl Betaine (Cocoamidopropyl dimethylglycine) Aerosol 30 by American Cyanamid Company, or Velvetex BA-35 by the Henkel Chemical Company.	16.00
Benzyl Alcohol	0.25

Continued

TABLE 10. (Continued)

Formula F (Continued)

Ingredients	% (w/w)
Methyl p.Hydroxybenzoate	0.25
PEG-150 [H-$(OCH_2-CH_2)_{150}OH$] Carbowax 8000 by Dow Chemical Company.	0.25
Fragrance	0.25
Deionized Water	37.00
Isobutane A-31 (Aeropres Corporation) (Propellant A-46)	5.10
Propane A-108 (Aeropres Corporation) (Propellant A-46)	0.90

Note: The first two ingredients may be replaced with 34.00% Disodium Oleamido PEG-2 Sulfosuccinate, 20.00% Sodium Laureth (3) Sulfate, and 2.00% Quaternium 22 substantive conditioner and humectant. The last item is available as Ceraphyl 60 from Van Dyk & Company, Inc.

Formula G

Easy-Spreading, Hair-Fixative Mousse

Ingredients	% (w/w)
Ethyl Ester of PVM/MA Copolymer (Gantrez ES-225, by the GAF Corporation; 50% A.I. in Ethanol)	5.00
Dimethicone Polyol (Surfactant 193 Fluid, by Dow-Corning Corporation)	0.50
Amino methyl propanol (95%) min.) AMP-95, by the IMC Corp.	0.20
Fragrance	0.20
Ethanol (Anhydrous Basis) S.D. Alcohol 40 (200°), by Publicker Industries, Inc.	10.00
Deionized Water	75.10
Isobutane A-31 (Technical Petroleum Company)	7.65

Continued

TABLE 10. (Continued)

Formula G (Continued)

Ingredients	% (w/w)
Propane A-108 (Technical Petroleum Company)	1.35

Note: The water-soluble 193 Surfactant acts to plasticize the copolymer and to enhance the spreadability of the resin on the hair. It also enhances foam building and foam stability. The possible need for a preservative should be investigated, although most of these formulas do not need one.

Formula H

Alcohol-Free Mousse for Damaged Hair

Ingredients	% (w/w)
Polyquaternium 11 (Gafquat 755N by GAF Corp.)	7.50
Blend of Trimethylsilylamodimeticone, Octoxynol 40, Isolaureth-6 and a glycol. (Dow-Corning Q2-7224; Dow-Corning Corporation)	1.00
Oleth-20 (PEG 20 Ether of Lauryl Alcohol) (Brij 98, by ICI Americas, Inc.)	0.50
Fragrance	0.20
Deionized Water	81.80
Isobutane A-31 (Technical Petroleum Company) (Propellant A-46)	7.65
Propane A-108 (Technical Petroleum Company) (Propellant A-46)	1.35

Note: The Dow-Corning Q2-7224 conditioning agent provides improved wet and dry combing and imparts a good handle or feel to the hair. The agent is particularly effective on damaged hair.

Combinations of about 3.0% Polyquaternium 11, 0.3% Polyquaternium 10, 0.3% Steareth 10 (Brij 76) and 0.15% PEG-2 Oleammonium Chloride (Ethoquad 0/12 - Armak) form a good base for alternative formulas. In some cases, up to 6.0% ethanol may be added.

Continued

TABLE 10. (Continued)

Formula I

Mousse Curl Activator

Ingredients	% (w/w)
Propylene Glycol	32.00
Isodecyl Oleate or Myristyl Myristate	4.00
C12-C15 Alcohols Lactate Ceraphyl 41 by Van Dyk & Co., Inc.	6.00
Glycerine	5.00
Quaternium-26 (Hydroxyethyl) Dimethyl (3-Mink animal oil amidopropyl) Chlorides. Ceraphyl 65 by Van Dyk & Co., Inc.	2.00
Quaternium-22 3-(D-Gluconoyl-amino)-N-(2-hydroxyethyl)-N,N-Dimethyl-1-propanaminium Chloride. Ceraphyl 60 by Van Dyk & Co., Inc.	1.50
Dimethacone Polyol Silicone Fluid L-720 by Union Carbide Corp.	1.50
PEG-40 Stearate Polyethylene Glycol (40 mol) Mono-ester of Stearic Acid	1.50
Cetyl Alcohol	0.50
Fragrance	0.25
Methyl p.Hydroxybenzoate Nipagin M by Nipa Laboratories, Ltd.	0.25
Deionized Water	40.50
Isobutane A-31 Phillips Petroleum Company (Propellant A-46)	0.75
Propane A-108 Phillips Petroleum Company (Propellant A-46)	4.25

Note: The propylene glycol and glycerine are hair curl activators, while the Isodecyl Oleate and C12-C15 Alcohols Lactate are glossing agents. The Quaternium 22 is an optional agent, used to increase humectancy and conditioning.

Four products were presented, with SPFs (Sun Protection Factors) of 2, 4, 6, and 12. For example, a product with an SPF of 12 will enable the user to remain in the sun twelve times as long as the standard period required to develop slight redness, while developing the same degree of coloration.

Since 1984, a number of relatively low-sales-volume sun screen mousse formulas have been launched. Some are identified as "sun screens;" others are labeled "sun and sport styling mousses" or other, less definitive names. Table 11 lists the ingredients of two strengths of typical sunscreen mousses.

Sun protection formulations with SPF values of 15 to 20 (the practical maximum) are often called sun-blocks (see Formula J in Table 11). They require combinations of sun-screen agents of the oil- and water-soluble type, to get the best distribution on the skin. In some cases, rigorous pH control, using buffering agents, is required. Concentrations of from 5.5 to 10.0% are required, depending on the efficiency of the screening agents, type of mousse emulsion, distribution on the skin, repeat applications, skin condition and moisture content, individual sensitivity, skin color, season, time of day, elevation, geographic latitude, type of activities, perspiration rate, product application thickness, etc.

For most people, a lesser degree of protection is acceptable. For those spending two or three hours in the sun at one time, the use of products with an SPF of about 4 to 6 is satisfactory. These products also permit the development of a tan, which is often socially important to those people or races having light-colored skin pigmentation.

Formula K, shown in Table 11, provides this intermediate degree of sun protection, based on the use of iso-amyl-p-methoxy-cinnamate. This water-insoluble material provides SPFs of 4 (at 2.8%), 6 (at 3.6%), 8 (at 4.5%), and 12 (at 7.5%). Thus, the formula can be adjusted to give whatever degree of solar protection is desired.

TABLE 11. SUNSCREEN MOUSSE FORMULATIONS

Formula J

Sunscreen Mousse (SPF About 15)

Ingredients	% (w/w)
Isodecyl Oleate or Myristyl Myristate Isodecyl Oleate is available from Van Dyk & Co., Inc. as Ceraphyl 140-A.	6.00
Octyl Dimethyl PABA (formerly Padamate 2) Ester of 2-Ethylhexyl Alcohol & Dimethyl p.aminobenzoic Acid Escalol 507 by Van Dyk & Co., Inc.	6.85
Benzophenone-3 2-Hydroxy-4-methoxybenzophenone Uvinol M40 by BASF-Wyandotte Chemical Company	3.20
Stearic Acid Octadeconoic Acid	10.00
Cetyl Alcohol Hexadecyl Alcohol	0.45
Deionized Water	44.95
Hydroxypropyl Methylcellulose Methocel F, by Dow Chemical Company, or Viscontran MHPC by Henkel Chemical Company	0.55
Propylene Glycol	2.50
Triethanolamine 99% Triethanolamine by Union Carbide Corp.	1.15
Ethanol Alcohol (Anhydrous Basis; Specially Denatured) S.D. Alcohol 40 by U.S. Industrial Chemicals Division	18.00

Continued

TABLE 11. (Continued)

Formula J (Continued)

Ingredients	% (w/w)
TEA Coco-Hydrolysed Animal Protein (and) Sorbitol Triethanolamine Salt of the condensation product of coconut acids and hydrolysed animal protein Maypon 4CT by Stepan Chemical Company	1.00
Methyl p.Hydroxybenzoic Acid	0.15
Perfume	0.20
Isobutane	4.25
Propane	0.75

Formula K

Sunscreen Mousse (SPF About 6)

Ingredients	% (w/w)
Steareth-10 PEG Ether of Stearyl Alcohol; $CH_3(CH_2)_{16}CH_2$-$(OCH_2CH_2)_{10}OH$ Brij 76, by ICI Americas, Inc.	0.80
PEG 150 Distearate Polyethylene Glycol (150) Diester of Stearic Acid Kessco X-211 by Armak Chemical Company, or Witconol L32-45 by Witco Organics Division.	0.60
Sodium Hyaluronate Sodium hyaluronate - high-molecular-weight polymer from animal protein (90% powder) by Tri-K Industries, Inc. (Reseller for Canadian Packers, Ltd.)	0.10
DMDM Hydantoin 1,3-Dimethylol-5,5-Dimethyl Hydantoin Dantoin DMDMH-55 (or Glydant) by Glyco Products, Inc.	1.10

Continued

TABLE 11. (Continued)

Formula K (Continued)	
Ingredients	% (w/w)
Quaternium 52 Dibutyl Sebacate Dehyquart SP, by Henkel Chemical Co.	8.50
Isoamyl Methoxycinnamate (CTFA) (FDA is pending) Isoamyl-p-methoxycinnamate (98% min.) Neo-Heliopan E1000 by Haarmann & Reimer Japan K.K.	3.60
Cyclomethicone Cyclic dimethylpoly (3 - 4) siloxane Silicone #344 Fluid by Dow-Corning Corporation	2.50
Dimethacone Copolyol (Water Soluble) Dimethylsiloxane, end-blocked with surfactant groups Silicone #193 Surfactant by Dow-Corning Corporation	0.25
Polysorbate 80 Mixed oleate esters of sorbitol and sorbitol anhydride; mostly the monoesters, with 20 moles of ethylene oxide Tween 80 by ICI Americas, Inc.	0.15
Polysorbate 20 Mixed laurate esters of sorbitol and sorbitol anhydride; mainly the monoesters, condensed with about 30 moles of ethylene oxide. Nikko TL10 or TL-10EX by Nikko Chemicals, Ltd. or Tween 20 by ICI Americas, Inc.	0.40
Olealkonium Chloride Oleyl-dimethyl-benzyl-ammonium Chloride Ammonyx KP by the Onyx Unit of Stepan Chemical Co.	0.10

Continued

TABLE 11. (Continued)

Formula K (Continued)	
Ingredients	% (w/w)
Nonoxynol-20 Ethoxylated (20)-p-n.nonylphenol Igepal CO-850 by GAF Corporation, or Tergitol NPX by Union Carbide Corporation	0.10
Aloe Vera Aloe Vera Extract - 100% Pure (90% A.I. Powder) Aloe Vera 100% by the Terry Corporation	0.10
Perfume	0.30
Methylchlorisothiazolinone, and Methylisothiazolinone Kathon CG by Rohm & Haas Company	0.10
Hydrofluorocarbon 152 1,1-Difluoroethane Dymel 152 by E.I. DuPont de Nemours & Company, Inc.	4.00
Isobutane Isobutane A-31 by Phillips Petroleum Company	2.00

The mousse presentation can also be used for baby care products. They avoid the spillage and application problems of other formulations. Table 12 lists the ingredients of these formulations.

Other commercial mousse products include a facial cleansing preparation based on very mild surfactants such as disodium cocoamido MIPA sulfosuccinate and sodium laureth sulfate, including Quaternium-22 to provide conditioning and emolliency. A facial makeup mousse uses a triethanolamine stearate and PEG-20 stearate emulsifier combination to spread a combination of pigments and emollients on the face to give an elegant matte finish. Hand creams are also available, again based on triethanolamine stearate and PEG fatty acid condensates as the emulsifier. Glycerin (5%) is included as a humectant. More recently, a cationic skin mousse has appeared that includes mink (animal) amidopropyl dimethylamine to provide a unique lubricity and skin feel. Several more interesting products are under intensive development.

The vaginal contraceptive foam is a product in the drug category that depends on foam stability and density. The preferred active ingredient is Nonoxynol 9, or nonyl-phenoxypolyoxyethylene ethanol. The formula for a mousse product of this type has been published, and a variation is presented as Formula N in Table 13.

Commercial formulas in the U.S. range from 8-12.5% of Nonoxynol 9, and all the aerosols are pressurized with about 8% of a blend of CFC-12 and CFC-114. An Amended New Drug Application (to the FDA) will be required before the propellant can be changed to hydrocarbon or other types. This process takes the FDA about 3 to 5 years to complete, since the entire NDA file must be reviewed whenever a change is made.

A mousse product is also available for the treatment of mastitis infections in the udder of cows. An example is presented in Table 14.

A similar formula, based on the use of Procaine Penicillin G, represents an anhydrous mousse system. Both formulas are designed for injection into the udder via the sphincter canals. CFC-12 and CFC-114 are used for the products

TABLE 12. BABY CARE MOUSSE FORMULATIONS

Formula L

Baby Oil Mousse

Ingredients	% (w/w)
Deionized Water	23.00
Mineral Oil - Medium Viscosity	30.00
Cetaryl Alcohol (and) Cetareth-20 C16-C18 Alcohols and C16-C18 Alcohol PEG 20 Ethers Macol 124 by the Mazer Chemical Company	10.00
Isodecyl Oleate and/or Myristyl Myristate Ceraphyl 140-A and/or Ceraphyl 424 by Van Dyk & Co., Inc.	10.00
Cyclomethicone Cyclic dimethylpoly (3-4) Siloxane Silicone #344 Fluid by Dow-Corning Corporation	3.35
Ethanol S.D. Alcohol 40 (Anhydrous) S.D. Alcohol 40 (200°) by U.S. Industrial Chemical Div.	12.00
Aloe Vera Aloe Vera Extract - 100% Pure (90% A.I. Powder) Aloe Vera 100% by the Terry Corporation	0.25
Perfume Perfume selected for mildness	0.25
Methyl p.Hydroxybenzoate Nipagin M by Nipa Laboratories, Ltd.	0.15
Hydrofluorocarbon 152 1,1-Difluoroethane Dymel 152 by E.I. DuPont de Nemours & Co., Inc.	8.00
Isobutane Isobutane A-31 by Phillips Petroleum Company	3.00

Continued

TABLE 12. (Continued)

Formula M

Baby Powder Mousse

Ingredients	% (w/w)
Deionized Water	35.70
Silica (Powder) Hi-Sil 233 Fumed Silica Anticaking Agent by PPG Industries, Inc.	0.30
Quaternium-26 (Hydroxyethyl)Dimethyl(3-Mink Animal Oil Amidopropyl) Chlorides Ceraphyl 65 by Van Dyk and Company, Inc.	2.00
PPG Laneth 50 Polyoxyethylene (50) polyoxypropylene (12) Lanolin Ether Solulan by Amerchol Products Unit	0.50
Cetyl Alcohol	0.40
Talc Talcum Powder - Impalpable Altalc 200	18.10
Ethanol S.D. Alcohol 40 (Anhydrous) S.D. Alcohol 40 (200°) by Shell Chemical Company	32.00
Perfume	0.20
Hydrofluorocarbon 152 1,1-Difluoroethane Dymel 152 by E.I. DuPont de Nemours & Co., Inc.	8.00
Isobutane Isobutane A-31 by Phillips Petroleum Company	2.80

TABLE 13. VAGINAL CONTRACEPTIVE MOUSSE

Formula N	
Ingredients	% (w/w)
Nonoxynol 9	8.0
Lauric/Myristic Acids	2.5
Stearic/Palmitic Acids	3.5
Triethanolamine	2.2
Glyceryl Monostearate[a]	2.5
Polyoxyethylene (20) Sorbitan Mono-oleate	2.5
Polyoxyethylene (20) Sorbitan Monolaurate	3.5
Polyethylene 600 Glycol[b]	1.5
Polyvinylpyrrolidone K-30[c]	1.0
Benzethonium Chloride, USP[d]	0.2
Deionized Water	67.6
Propellant A-46	5.0

[a]Viscosity builder and foam stabilizer.

[b]Average molecular weight is about 600.

[c]Protective colloid.

[d]Benzyldimethyl [2-[2-(p.1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl] Ammonium Chloride

TABLE 14. MOUSSE FOR MASTITIS TREATMENT

Formula O	
Ingredients	% (w/w)
Sodium Lauryl Sulfate (30% Active Ingredient in Water) (As Duponol WA Paste, or equivalent)	27.7
Polyethyleneglycol 400 Distearate	3.5
Triton X-100[a]	0.4
Sodium Palmitate/Stearate	0.4
Sodium Sulfate 10-Hydrate	0.2
Sodium Citrate ½-Hydrate[b]	1.5
Neomycin Sulfate (as base)	3.8
Sodium Hydroxide (50% in Water) -- to pH 9.2	q.s.[c]
Deionized Water	56.5
Propellant A-46	6.0

[a]Foam modifier.

[b]Sequestrant and stabilizer.

[c]A sufficient quantity.

available in the U.S., but an interesting topical product, using dimethyl ether as the propellant was patented about 1984. It contains chlorhexidene acetate or gluconate plus a light-blue dye (to show the areas treated), in a hydroalcoholic system. After milking, it is used as a germicide and the chilling effect of evaporating diethyl ether causes the sphincter muscle to immediately close, preventing contamination of the udder quadrants and incidentally also preventing some leakage of milk. The product is especially useful for older cows on automatic milking machines.

Pharmaceutical foams have been well received for over a dozen specific applications, including hemorrhoid treatment, relief of tenesmus in deep wounds and ear cleansing.

When foam medicinals are to be inserted into various body cavities, it is often best to use a special type of very blunt, all-plastic syringe, such as the model shown in Figure 1.

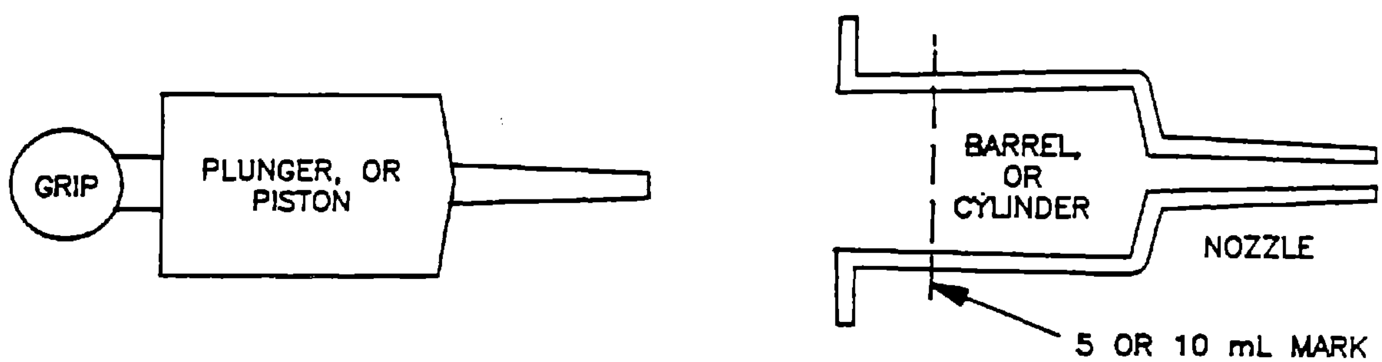


Figure 1. Foam Syringe

Directions: To use the metering syringe, fill the barrel with foam to a level beyond the volume mark, minimizing any air pockets. Press the piston in until it reaches the volume mark, removing excess from the nozzle tip. Insert; then slowly press the piston in to the fullest extent. The narrow tip of the plunger serves to minimize any wasted product remaining in the nozzle area, since such medications are often rather costly.

Since dosage is directly affected by foam density, it is desirable to formulate a foam with a density in the range of 0.05 to 0.10 g/mL, using sufficient propellant so that the foam density at the beginning of product use will not be more than 25% less than that near the end. Uniformity of propellant fill is also very important. For example, a Pamasol "Stepped Rotary" filler contains two concentrate filler heads, a crimper, and two propellant filling heads. It will produce 35-40 meter-spray cans per minute, or 60-70 regular cans per minute, filling both product and propellant with good accuracy. It is the filler of choice (worldwide) for small, pharmaceutical products.

Shave Creams

Shaving creams--the last of the "mousse" products to be discussed--are more of a utility product than a personal care item. In the U.S., a 310-g dispenser can still be purchased on sale for less than $1.00, although most of the name-brand shave creams cost at least twice that much.

Discovered in 1931 by Eric Andreas Rotheim of Norway, who pressurized certain soap solutions with butanes, the shave cream was reborn in the U.S. in 1948. It used from 6.5 to 8.5% of a CFC-12/114 blend. In 1954, all but one marketer changed over to 3.4 to 4.0% Propellant A-46. This particular blend of propane and isobutane has air-free pressures of 3.24 $\pm$ 0.14 bar at 21°C, and 8.87 $\pm$ 0.35 bar at 54.4°C. At the time of its first production, it was the highest-pressure mixture that could be used for atmospherically crimped, standard-strength aerosol cans. Table 15 gives the formulations for three typical shave creams.

The usual shave cream formula is an 8 to 12% dispersion of sodium or potassium and triethanolamine fatty acid soaps in water, plus foam stabilizers, wetting agents, emollients, humectants, fragrance, preservatives, and sometimes special ingredients. Some fairly exotic materials have sometimes been used, such as fluoro-acrylic "super-detergents" for extra beard softening, and hyaluronic acid, a natural polymer that encourages the skin

TABLE 15. SHAVE CREAMS

Ingredients	Formula A	Formula B	Formula C	U.S. Tradenames
Deionized Water	74.9	79.5	78.1	
Lauric/Myristic Acids	1.5	1.0	0.7	Emersol 132,et.al.
Stearic Acid (Triple X)	6.0	7.0	8.0	Emersol 655 or 621
Lauryl/Myristyl Diethan-olamine	0.5	2.0	----	Schercomid SLM-S
Sodium Lauryl Sulfate (30% Water Solution)	----	----	1.5	Duponol WAT 30%
Sodium Hydroxide (50%)	----	0.5	----	Dow Chemical Co.
Potassium Hydroxide (45%)	----	2.25	0.4	
Triethanolamine (99%)	3.9	----	3.0	Union Carbide Corp.
Cetyl Alcohol, N.F.	0.5	----	----	
Glycerin - 96%, U.S.P.	5.8	4.0	2.5	
Polyvinylpyrrolidone K30	----	0.15	----	
Mineral Oil, N.F. Grade	2.4	----	----	Witco "Carnation"
Methyl p.Hydroxybenzoate	0.1	----	0.1	
n.Propyl p.Hydroxybenzoate	0.03	----	0.04	
Fragrance	0.67	0.3	0.36	IFF #2651-AB
Lanolin Derivative	0.5	0.2	2.0	Lantrol-Malmstrom
Propellant A-46	3.2	3.1	3.3	Phillips Petroleum

Note: These formulas may be packaged in tinplate or aluminum single-lined cans.

renewal process and moisturizes the skin, to reduce the irritation of close shaving.

Formula A is the highest quality of the three, followed by Formula C. Formula A is also the most costly, but the marketer has the option of making such claims as "sodium free," "contains no alkali," or "100% organic," which may be advantageous.

In addition to the foam stability provided by the sodium lauryl sulfate (often called SLS), PVP K30, lauryl/myristyl diethanolamide (or coco-diethanolamide), and especially cetyl alcohol, formulation chemists may use Keltrol or Methocel 25MC thickeners, Monamid 150LW, Deriphat 170-C (acid zwitterion) and other ingredients. The critical test for sufficient foam stability is that the foam should not significantly drain or dry out from below the nose of the user in less than three to four minutes, even at low humidities. It should also be stiff, smooth and thick-textured, and form a 5-g puff able to support a full-length pencil at a 5° angle. Some foams are dispensed hot, either using reactive chemicals (such as sodium thiosulfate and 10% hydrogen peroxide, kept separate until the moment of use), or more commonly by using an electrical heating mantle. In such cases, the foam may be delivered "steaming hot" at up to 85°C, and quite a lot of extra foam stability agent will be required. These hot foams represent only about 4% of the 210,000,000-unit U.S. aerosol shave cream market.

The choice of propellant is critical to success. At pressures of 2.5 bar or less at 21°C, a secondary expansion will occur in the hand, which is perplexing to the user. Blends higher in pressure than Propellant A-46 will normally require a special, high-pressure-resistant can.

The amount of propellant is also important to success. The use of too little propellant results in production of a higher density foam (such as 0.12 g/mL), and the situation will worsen as the dispenser is used up. This is because emulsified propellant can escape into the expanding head space, leaving less in the liquid phase to produce the foam structure. Conversely, over 4.0% hydrocarbon propellant will produce a relatively dry, airy foam with poor wetability and smooth-out properties. Excessive propellant may escape during actuation, leaving the foam puff defaced, with a pock-marked, wrinkled or roughened surface. The noise level will be higher as the propellant tears the foam micro-structure during the escape process.

Some work has been done with alternative propellants. Those with both oil and some water solubility produce less stable foams, such as HFC-152a, but the stability may be adjusted by using blends of HFC-152a and hydrocarbon propellant. Dimethyl ether will not produce a foam. Nitrous oxide generates satiny foams with very fine micelle structures, as does carbon dioxide. Despite the low solubility (about 1%), these foams remain reasonably uniform throughout package life, especially if only 60-65% product is placed in the can.

Many unusual foams have been produced. There are exploding foams, bouncing types, crackling foams, and even anhydrous foams of astonishing durability. Several anhydrous types are used for the application of topical pharmaceuticals.

Several food foams have been introduced, but the only really successful one is whipped cream, which is nearly always pressurized with approximately 1.2% nitrous oxide. The slow growth of psychrophilic bacteria, even at 2°C, has posed a major shelf-life problem for many of these products. One U.S. filler has developed a process for producing sterile products, but enzymes will adversely affect even these products within a few months.

Whipped food products that have not been marketed to any extent are pancakes (crepes), expanded mayonnaise, whipped syrups, ice cream toppings, chocolate milk additives, and alcoholic toppings for Irish Coffee and certain mixed drinks. In the U.S., the hydrocarbon propellants, nitrous oxide, carbon dioxide, and nitrogen, are the only propellants permitted for food uses. In some other countries, nitrous oxide is not allowed in food products. One of the key problems with food aerosols is that the final dispensers cannot be autoclaved to render the contents sterile without causing the cans to burst.

Underarm Products

In the U.S., these aerosol products fall into two distinct classes: the antiperspirant and the deodorant. Antiperspirants are considered drug products by the U.S. Food and Drug Administration because they have a definite physiological effect on the pores of the skin, and they are regulated accordingly. On the other hand, a simple deodorant consists of an alcoholic solution of a germicide, which does nothing except to reduce the population of skin resident bacteria for several hours, thus inhibiting their ability to degrade certain ingredients in natural perspiration into malodorous materials. Antiperspirants also function as deodorants, because they reduce the pH value of the skin to about 3.2 to 4.2 at 35°C, and this level of acidity inhibits the proliferation of microorganisms.

In the U.S., an aerosol antiperspirant must, by definition, act to reduce the rate of perspiration. More specifically, antiperspirants must reduce the output of the apocrine sweat glands by twenty to seventy per cent. These glands are actually located not only at the armpits, but in the ano-genital area, the eyebrows, and (in women) behind the ears. Despite the commercialization of aerosol antiperspirants in the past for more general body application, currently available products are labeled for underarm use only.

All antiperspirants have a physiological effect on the skin, but these effects vary widely with the formula, the consumer, testing conditions, time, and other factors. Sweat reductions even between the right and left underarm areas of a given person may be quite different. In 1978, the FDA issued a set of OTC (Over-The-Counter) drug regulations for antiperspirants, titled "Guidelines For Effective Testing of OTC Antiperspirants" that defined an axillary sweat reduction study (2) as a proposed Monograph. It stipulated that an aerosol antiperspirant must reduce sweat by at least 20% after both 1 hour and 24 hours from the time of application in at least 50% of a minimum 15-person target population. The test conditions were 38°C and 35% RH (Relative Humidity) during the one-hour collection periods for each day of the five-day test cycle, and 22.2°C otherwise. Application time was described as a two-second spray under each arm.

Until the introduction of the more powerful aluminum chlorohydrate complexes in 1986, most aerosol antiperspirants fell into the 22-33% sweat reduction category. By comparison, stick antiperspirants exceed 40% and some roll-ons reach 65%. However, a sweat reduction of 25% or more represents such a dramatic improvement in the control of wetness that many users are quite satisfied with aerosol performance. During the recent introduction of the new, more potent antiperspirant materials, however, the suppliers stated that they made these changes because of some user dissatisfaction with product effectiveness, resulting in a sales reduction of the aerosol category over the years. Aerosol antiperspirants have also had modest problems with "bounce off," resulting in some nasal irritation, higher packaging costs, and occasional valve plugging. Recent attempts to reduce ground-level ozone (smog-related) have caused at least one state to study aerosol VOC emissions.

During 1985, the Reheis Chemical Company (U.S.) announced their new line of REACH antiperspirants for aerosols and other dispensing forms. These are up to 50% more potent than the standard aluminum chlorohydrate complex; e.g., $[Al_2(OH)_5]_{13} \cdot 2.5H_2O$--which has an Al:Cl ratio between 2.1 and 1.9 to 1.0, and an FDA permit level of up to 25% of the total product.

The new REACH 101, 201, and 501 compositions represent commercial forms of aluminum chlorohydrate polymer that can be separated out of the mixture of polymers in the parent compound using liquid chromatography. The Al:Cl ratio is maintained. With the greater effectiveness (up 30 to 50%, depending on choice) formulators had the following options:

- Use the new compounds at the former levels, for a 30 to 50% more effective product; or
- Use reduced concentrations of the new compound, lowering the effectiveness of the product to the former level, but reducing formula cost and bounce off.

Table 16 compares some representative antiperspirant product efficiencies.

In one form or another, aluminum chlorohydrate is the only active material now used in aerosol products, but the specific polymeric compositions and their particle size distributions have gone through a transition from 1986 through 1989 that now suggest that the REACH compounds have captured at least 80% of the U.S. market volume. In 1988, the aerosol underarm products sold increased from 114 million units to 144 million, or 26%, although the aerosol industry grew by a comparatively small 6.8 percent. This extraordinary growth is said to have been the result of the availability of more effective products and well-advertised introductions by Mennen, Bristol-Myers, and other marketers. The aerosol share of the underarm market also grew, from 31% to 37%.

The present products contain from 7.0 to 12.5% of various aluminum chlorohydrate complexes. Without the addition of a dispersing system, the suspended aluminum chlorohydrate would settle into a bottom layer between uses and would require long and difficult shaking to redisperse. Also, the material within the very bottom of the dip tube will not redisperse even with shaking, leading to valve plugging and consumer dissatisfaction. Because of this, all aerosol antiperspirant formulas contain a dispersing agent, normally a surface-treated form of montmorrillonite clay activated by the inclusion of a relatively polar ingredient such as ethyl carbonate or ethanol. With the correct combinations and balances and good compounding techniques, clogging problems can be avoided.

Table 17 presents the formulation of a low-cost, low "bounce off" antiperspirant of above average effectiveness.

Both the isopropyl myristate and silicone fluids of the formula shown in Table 17 are useful as inert carriers to transport the aluminum chlorohydrate to the skin surface and stick it there with a minimum of bounce off. These ingredients are also needed as slurrying material for the aluminum chlorohydrate to facilitate the production process.

TABLE 16. COMPARISON OF ANTIPERSPIRANT EFFICIENCIES

Generalized Composition and Form		% Efficiency First Day	% Efficiency Fourth Day
3.5%	Old CFC Formula (Banned in 1978)	25	
10.0%	Hydrocarbon-Type Aerosol	25 $\pm$ 7	29 $\pm$ 7
12.5%	Hydrocarbon-Type Aerosol	30	
10.0%	Hydrocarbon-Type Aerosol (REACH 101)	44 $\pm$ 8	57 $\pm$ 6
10.0%	Hydrocarbon-Type Aerosol (REACH 201)	38 $\pm$ 8	50 $\pm$ 9
10.0%	Hydrocarbon-Type Aerosol (REACH 501)	35 $\pm$ 7	45 $\pm$ 10
20.0%	Suspension Stick - Standard	40	
20.0%	Suspension Stick - Rezal 36GP Active	55	
25.0%	Roll-On Suspension - REACH AZP-703	62	

TABLE 17. AEROSOL ANTIPERSPIRANT

Ingredients	% (w/w)
Aluminum Chlorohydrate (REACH 101)[a]	8.00
Quaternium 18 Hectorite (Bentonite 38)[b]	0.82
S.D. Alcohol 40-2 (Anhydrous)	0.80
Dimethylsilicone [500 centistokes (cstks)][c]	1.50
Isopropyl Myristate[d]	1.00
Cyclomethicone F-251[e]	7.63
Perfume Oil[f]	0.25
Propellant A-31 or A-46[g]	80.00

[a]REACH 101 is produced by the Reheis Chemical Company, 235 Snyder Avenue, Berkeley Heights, NJ. (201)464- 1500. (An equivalent product is produced by the Wickhen Division of the Dow-Corning Corporation.)

[b]Bentonite 38 is a surface quaternized form of montmorillonite clay, offered by NL Industries, Inc. as "Bentone 38."

[c]Dimethylsilicone (500 cstks.) is available from Dow-Corning Corp., General Electric Silicones Division, and others. Purchase the anhydrous (clear) liquid, not the emulsion forms.

[d]Isopropyl Myristate is sold by Van Dyk & Co., Inc. and many other firms.

[e]Cyclomethicone F-251 is a physical mixture of Cyclomethicone D-4 Tetramer 25%, and Cyclomethicone D-5 Pentamer 75%. It is available from the Dow-Corning Corp.

[f]The perfume oil is the marketer's choice. It must be purchased from a perfume house that is advised that it will be used in a REACH 101 aerosol antiperspirant, and then tested for compatibility with the product. The percentage may vary, according to fragrance intensity and the marketer's preference.

[g]Propellant A-31 (with vacuum crimp) is preferred, giving a can pressure of about 2.5 bar at 21.1°C. The use of Propellant A-46 will provide an initial pressure of about 3.6 bar at 21.1°C (with vacuum crimp) and thus a delivery rate approximately 19% faster at the beginning of use. Preferential removal of air and propane through the vapor-tap orifice will reduce pressure to about 2.6 bar at 21.1°C when the dispenser is 50% empty, and to about 2.3 bar at 21.1°C at the point of incipient emptiness.

(Continued)

TABLE 17. (Continued)

Notes:

1. Concentrate Viscosity: 18,000 cps. (Brookfield Viscometer; 10 rpm.)

2. Concentrate pH Value: 3.3 - 4.7 (1:10 v. dilution in deionized water)

3. Concentrate must be homogenized to remove probable clumps or clusters of oil-wetted aluminum chlorohydrate powder.

4. REACH 101 is hygroscopic and must be protected from the moisture in ambient air at all times. Once it is added to the oily concentrate it will no longer absorb moisture. The following recommendations apply:

   - Keep drums closed except when sampling or using;

   - Do not remove packets of moisture-absorbent silica gel in drums, if present, except when adding REACH 101 to batch;

   - Add REACH 101 as quickly as practical, while still minimizing clumping; and

   - Rinse off tank walls of REACH 101 powder, immediately after addition.

5. If a U-t-C (Under-the-Cap) gasser is used, the last 10% of the propellant must be added by means of a following T-t-V (Through-the-Valve) gasser in order to clear thick concentrate from the dip tube and avoid possible valve-plugging problems.

6. All equipment touching the concentrate should be of 304 or 316 stainless steel, Tygon® hose, or approved rubber hoses in good condition.

7. The concentrate is sufficiently thick or viscous that settling of the solids will be a slow process. However, continuous recycling of the concentrate is required, as well as some slow stirring of the concentrate filler bowl. Over-circulation, such as short-loop circulation during filler downtimes, is not recommended. It may cause localized heating and micro-splintering of the solid aluminum chlorohydrate.

The isopropyl myristate improves feel (or handle) and texture. Being essentially nonvolatile, it helps the Dimethylsilicone (500 cstks.) carrier keep the underarm area lubricated for many hours.

The other silicone materials are relatively volatile. The F-251 blend is selected for a combination of effectiveness and lower expense. They are used to impart an extra measure of carrying ability and skin lubricity, preventing any tackiness development as the aluminum chlorohydrate slowly dissolves in perspiration films. Having done their work, they slowly evaporate, preventing long-term excessive oiliness and the staining of clothing in the underarm area.

The isopropyl myristate, and various silicone fluids also help the operation of the aerosol powder valve. They reduce the amount of bulking agent needed to prevent hard-packing of solids between product applications. Finally, they provide spreading characteristics that help distribute the aluminum chlorohydrate more effectively across the dermal surface.

If excessive amounts are used, the oil may coat the aluminum chlorohydrate so effectively that it cannot contact skin moisture and begin dissolving. This will cause a lag between the time of application and the time antiperspirancy becomes apparent. Fabric staining, "wetness," and cost will all increase if too much isopropyl alcohol and silicone fluids are used.

Other materials have been suggested as replacements for these ingredients. For example, Croda, Inc. suggests replacing isopropyl myristate with their Procetyl AWS (a propoxylated/ethoxylated ether of cetyl alcohol). Union Carbide suggests using Fluid AP, and others have promoted such items as myristyl myristate ester and octyl palmitate ester. Such ingredients are added at some risk. For example, some samples of myristyl myristate contain small amounts of unreacted myristic acid, which can seriously reduce or even eliminate the antiperspirancy of the aluminum chlorohydrate.

The Bentone 38 surface-polarized montmorillonite clay is very finely divided and has the approximate formula $NaCa[(Al,Mg)_2Si_4O_{10}]\cdot Q\cdot nH_2O$, where Q is a specific quaternary ammonium compound designed to increase surface charge and further promote suspending properties. A small amount of ethanol is added to activate the polar surface and augment charge separation.

When the balance is achieved, the Bentone 38 and ethanol system will slow down the settling of the aluminum chlorohydrate and allow it to eventually settle into a lose, voluminous layer between product uses. A gentle inversion or shake will then swirl the solids back into suspension. This should be checked for any new formula (even a new perfume in a tested formula) using glass compatibility equipment. If the aluminum salts can settle into a hard, obdurate mass--regardless of settling rate--the product will suffer from problems of reconstitution and probable valve plugging.

Both scented and unscented antiperspirants are marketed. The unscented versions are sometimes preferred by men, and always by hypoallergenic persons. They are usually very lightly scented, despite the label, using approximately 0.04% of nondescript perfume oils to cover the slight chemical odors of the other ingredients. Some products contain encapsulated perfumes, in addition to the "non-encap" perfume. They provide longer-term fragrance release, as moisture dissolves the modified polyvinyl alcohol (0.001"(0.025mm)-diameter) micro-capsules of additional fragrance.

The aluminum chlorohydrate easily develops enough acidity under the arm to prevent the proliferation of skin-resident, odor-causing bacteria. Thus, no special microbicides need be added, except to treat cases of chronic hyperhydrosis or certain other dermal pseudomorphoses.

The homogenization step for the concentrate-processing stage should be a one-stage, rather gentle one designed to break up clusters of oil-saturated aluminum chlorohydrate, rather than to fracture the roundels of the salt itself.

The roundels are already sufficiently fine-particled that they will not clog an aerosol valve. But if they are broken up into a lot of "splinters," buildup and possible clogging might occur.

Sample amounts of the concentrate should be made in the laboratory so that the viscosity and flow characteristics of the batch-making process can be considered. A variable speed, planetary, top-entering agitation system is needed for best results. When the powder is added and viscosity increases, all parts of the mixture must be agitated.

The compounding procedure is as follows:

- Add the isopropyl myristate, through a 5-micron filter;

- Add the Cyclomethicone F-251, through a 60- to 100-mesh screen;

- Begin agitation at about 75 rpm;

- Begin recycling, out the bottom and back into the tank via a pipe that extends to the lower one-third, to prevent splashing. The pump in this system should be set at around 150 to 200 rpm to prevent shearing. A Cuno or similar filter in this line will be bypassed during the compounding stages;

- Pre-weigh the Bentone 38 and add manually to the tank at a fairly slow rate, about one 20-kg bag per minute at most;

- Agitate at least 15 minutes, until the Bentone 38 is dispersed;

- Add the SD Alcohol 40-2 (Anhydrous);

- Operators in face masks and protective clothing then add powdered aluminum chlorohydrate REACH 101 to the mix-tank at a rate of about 25 to 50 kgs per minute:

    -- Build batch size around full-drum amounts of REACH 101 if possible, to prevent dealing with partial drums,

-- Protective masks and clothing are needed because of the generation of irritating dusts during additions;

- Rather quickly, add the dimethylsilicone (500 cstks) to the batch tank, using a suitable Tygon or rubber hose, so that deposited powder on the walls and dome of the mix-tank can be rinsed down into the batch;

- Add Perfume Oil;

- Agitate at least 15 minutes. Check for dispersion uniformity;

- Arrange recycling line to pass product through stainless steel Cuno filter (coarse) and through either a Votator or Homogenizer to homogenize the lumps. Use a filter with about 0.13-mm spacings. Use a flow rate of 150 to 200 kg per minute;

- Pass the finished concentrate into a stainless steel, agitated holding tank, with a recycling line as close to the concentrate filler as practical. The temperature will have increased some 5° to 10°C during rotating or homogenizing, but it should not be allowed to be over 40°C.

The valve is often supplied by Precision, Seaquist, Valois, Aeroval, Summit, or other major manufacturers in a rounded edge, powder-valve design. In the U.S., a large, 20-mm diameter, white, one-piece button is used. It is ordered separately from the valve and applied by hand (rarely) or by an automatic button tipper, often to line up with the 180° reverse-directional dot on the crown of the valve cup.

A prototype valve is one with a 0.46-mm stem orifice, 0.63 x 0.46-mm vapor-tap body, neoprene gasket, and 0.50-mm straight-bore actuator button. The delivery rate can be changed downward if desired by using a 0.50-mm vapor-tap orifice instead of the 0.46-mm size. Many formulators check several larger-volume products on the market and decide which ones have the best spray pattern, delivery rate, and other characteristics they require. They then contact the appropriate valve company, identifying the product, and ask for a sample valve made to the same specifications. Unless it is a customized component (which is rare, except perhaps for color) the valve-maker will always comply.

Two forms of the REACH 101 antiperspirant powder, differing only in particle size distribution, have been used in aerosols:

- MICRO-DRY "REACH 101" (Reheis): Standard. Impalpable. More than 99.8% of the particles are smaller than 74μ;
- MICRO-DRY "REACH 101" (Reheis): Ultrafine. At least 99.8% of the particles are smaller than 50μ.

A filtration step, using a Cuno or equivalent cartridge filter of 0.13-mm retention, removes agglomerates, oversized particles, tramp cellulose fibers (from bags), and other extraneous solids from the finished batch of concentrate. Experience suggests that the Standard, Impalpable grade is quite satisfactory and somewhat less of a potential problem in terms of the rate of moisture pickup during handling. However, it is always a good idea to contact the suppliers (Reheis and Dow-Corning Corporation, in the U.S.) and ask for recommendations and literature.

The aerosol can may be a necked-in 200-201/202x406 or 509 or 514-mm can in the U.S. market, which is equivalent to a 51-51/52x111 or 140 or 148-mm can elsewhere. The necked-in version is a marketer preference, based mainly on aesthetics, not on technical or functional requirements. The so-called "straight-wall" cans are also acceptable. Because the low-density hydrocarbon propellants are nearly always used at levels approximating 75%, it is customary to place a 100-to 115-gram fill weight into the can size just described.

In the U.S., the necked-in cans have a 50.70 ± 0.25-mm industry specification for the diameter of the top double seam. This relatively difficult specification reflects a need for uniformity to prevent full-diameter straight-wall cover-caps from fitting too tightly or too loosely when applied over the seam.

The cans are generally of minimal tinplate throughout, with a single lining and usually a stripe over the welded side seam. Adherence to Good Manufacturing Practices (GMP), which includes code legibility, is a general requirement for this Over-The-Counter drug product.

The personal deodorant (or underarm spray deodorant) complements the antiperspirant. It is often used by those who have either constant or sporadic skin irritation problems with antiperspirants because of their salinity, astringency or acidity, or by those for whom underarm perspiration is either not a problem, or cannot be controlled by antiperspirants because of the environment or type of activity.

The basic personal deodorant formula consists of a germicide, fragrance, ethanol solvent, deionized water (sometimes) and propellant. The standard propellant in the U.S. is either isobutane, or a mixture of up to 37 wt% propane in isobutane. In Europe, both hydrocarbon and dimethyl ether propellants have been used. Various HFC and HCFC propellants could technically be used, but their higher cost has so far effectively precluded their use. Four representative formulations are given in Table 18.

The size of the personal deodorant market is now about 55,000,000 units in the U.S., 34,700,000 in 1988 in Japan, and relatively small in Europe. The containers are similar in size and logo to the antiperspirant aerosols, and are sometimes purchased by mistake because of this. Most major marketers offer both products in two or three sizes and in both scented and unscented

TABLE 18. PERSONAL DEODORANTS

Ingredients	Formula A (%)	Formula B (%)	Formula C (%)	Formula D (%)
Irgasan DP-3000[a] Germicide	0.11	----	----	0.12
Genzthionium Chloride[b]	----	0.20	----	----
Methyl p.Hydroxybenzoate	----	----	0.03	----
n.Propyl p.Hydroxybenzoate	----	----	0.06	----
Benzyl p.Hydroxybenzoate	----	----	0.08	----
Propylene Glycol, U.S.P.	1.50	----	1.03	----
Dipropylene Glycol	----	1.05	----	2.00
Zinc Phenolsulfonate[c]	----	----	----	1.00
Fragrance	0.35	0.25	0.30	0.38
S.D. Alcohol 40-2 (Anhydrous)	58.00	68.50	63.50	13.35
Deionized Water	----	----	----	47.00
Sodium Benzoate	----	----	----	0.15
Isobutane (A-31)	40.00	----	----	----
Propellant Blend A-46 16 wt% Propane in Isobutane	----	----	35.00	----
Propellant Blend A-70 37 wt% Propane in Isobutane	----	30.00	----	----
Dimethyl Ether	----	----	----	36.00

[a]2,4,4'-Trichloro-2'-hydroxydiphenylether.

[b]Benzyldimethyl [2-[2-(p.1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl] Ammonium Chloride.

[c]Zinc Sulfocarbolate.

versions. The packaging requirements for the hydrocarbon-propelled formulas are designed to give a fairly fine-particled, low delivery rate spray, using a vapor-tap valve with (typically) a 0.33-mm diameter orifice and a mechanical break-up button. For the dimethyl ether products (as in Formula D of Table 18), very efficient valves are required to break up the large amount of water present. The Precision Valve Corporation's 2 x 0.50-mm "Aquasol" stem valve, 0.50-mm MBST (Mechanical Break-Up, Straight Taper) button, and butyl rubber stem gasket valve may be used. The supplier should be contacted for specific recommendations, but sprays of 60μ average particle size are obtainable. The somewhat higher cost of dimethyl ether in most areas can be justified by its ability to incorporate significant amounts of water in solution, giving the feeling of excessive wetness. The flame projection of this formula will vary somewhat with valve selection, but it is generally a 100- to 150-mm small, sputtering light blue plume or flare.

Colognes and Perfumes

A cologne is generally considered to be a dilute form of the perfume or sachet product, containing from 1.5 to 6.5% of essential oil or fragrance compound. The true perfume may contain from 6.5 to 14.0 percent. The carrier is almost always ethanol, generally anhydrous ethanol, and the propellent is often a hydrocarbon type. For perfumes, which are smaller and more costly than colognes, the glass or aluminum dispenser carries a meter-spray valve able to dispense about 0.05 gram per actuation. A typical 20-gram fill will offer about 400 actuations to the user.

The European innovation known as the deo-spray is a form of cologne and has the typical cologne composition. No deodorant is present, as might be inferred from the generic name. Packaged in lined aluminum cans holding as much as 200 grams, the deo-spray or deo-cologne provides an inexpensive option for spraying one's skin or clothing with a relatively low-cost but still acceptable fragrance. Some deo-sprays are made especially for use by younger children and are labeled accordingly. Plastic caps resembling flowers and animal heads have been used for added appeal. Finally, the sachet spray falls somewhere between a cologne and a perfume. It contains approximately 4 to 8%

fragrance compound formulated to as light a color as possible to prevent the staining of lingerie, handkerchiefs, and other fabrics. Two typical cologne formulas are presented in Table 19.

Glass has been the accepted standard for colognes since the origin of the aerosol cologne in 1953. While plain glass containers of up to 125-mL capacity have been marketed, glass bottles of greater than 30-mL capacity are usually plastic coated. In the U.S., the Wheaton Aerosol Company's "Lamisol" container is often used. It has a vinyl-based covering that firmly adheres to the glass surface, making it more resistant to fracturing if dropped and helping to contain glass fragments and flammable vapors if the container does break. At present, the U.S. Department of Transportation limits the size of non-metallic aerosol dispensers to a capacity of 118.3 mL (without a special exemption).

The use of the OPET, Petasol, and similar plastic bottles is being studied in the U.S., Japan, and Europe. Based on biaxially-oriented polyethylene terephthalate, these bottles offer lightness, great break resistance, clarity, translucency, or opacity, and more freedom of shape and design than glass. Their very lightness has been viewed as a marketing deterrant, since buyers are accustomed to the solidity and weightiness of glass as a quality attribute. These bottles cannot be used for strong solvents, such as dimethyl ether, since they lose strength rather rapidly at temperatures of over 60°C, and may suffer from permeation effects when used with some formulations. In England, hair sprays (not too different from many cologne formulas) have been marketed successfully as 200-gram fills in OPET bottles.

The levels of HFC-152a ($CH_3 \cdot CHF_2$) or HCFC-22 ($CHClF_2$) used in Formula A in Table 19 are considered minimum levels. The vapor pressures of both propellants are suppressed when they are added to ethanol, an effect reduced when water is incorporated as a third ingredient. This is why Formula A contains 13% deionized water. An aerosol valve with maximum breakup power is used for all cologne formulations.

TABLE 19. COLOGNE FORMULATIONS

Ingredients	Formula A (%)	Formula B (%)
Fragrance	4.00	4.00
Di-n.butyl Phthalate	2.00	----
Sodium Saccharinate[a]	0.01	----
FD&C and/or D&C Dye Solution[b]	0.09	----
S.D. Alcohol 40 or 39C (Anhydrous)	65.00	76.00
Deionized Water	13.00	----
HFC-152a or HCFC-22	15.90	----
Isobutane A-31	----	20.00
Packaging mode:	Glass	Aluminum

[a]The Sodium Saccarinate (or a similar synthetic sweetener) is added to nullify the rather tart bouquet of the ethanol.

[b]In the U.S., these are Food, Drug, and Cosmetic-approved dyes or Drug and Cosmetic-approved dyes in the form of a stock solution of various concentrations. The solvent is generally deionized water, but propylene glycol and/or a preservative may be added as well.

Perfumes, deo-sprays, sachets, and related products have relatively similar formulations. Fragrance is deposited on an animate or inanimate surface with high efficiency. The spray must be relatively wet, but still retain cosmetic elegance.

Although dimethyl ether could be used in fragrance products, and there are those who claim it imparts a cleaner, fresher odor, especially when water is included, others suggest that the propellant itself has a stronger odor than the purified hydrocarbons, and certainly much higher than HFC-152a, which has almost no odor at all. Fillers in various parts of the world continue to use CFC-12/114 blends for perfumes and colognes, partly because of the greater importance of reduced final-product flammability when dealing with a frangible material such as glass. Some of these fillers are not set up yet to safely handle flammable propellants. In time, they will have the option of converting to nonflammable HCFC-22 propellant or to one of the nonflammable future alternative types, such as HFC-134a. The latter is a modest solvent and is virtually odorless.

Perfumes are extremely complex mixtures of both natural and synthetic materials, and it is rare that all of them are soluble in the complete aerosol formula. In some instances, these resinous substantives will only precipitate after several days or weeks. When they do, they usually agglomerate into fairly hard masses, readily capable of causing sputtering, distorted spray patterns or even plugging the aerosol valve. In a clear glass container the precipitation can be seen, and it gives a very negative image of product quality.

An early industry practice was to store the complete formulation in a covered 2,000-liter tank at -10°C for several days, then to filter out the dregs enroute to the product filler. With the flammable propellants, this technique is no longer practical, although the complete concentrate can certainly be held for a time at room temperature and then filtered free of precipitates. The perfume suppliers are well aware of the problem and can sometimes provide fragrances that have been tested to show that the addition of hydrocarbon propellants to the filtered concentrate will not cause any further precipitation. The marketer should always make the "two-week test," which is to prepare the finished formula in either a clear glass aerosol, or in a clear glass product-compatibility tube of about 100-mL capacity, holding it for one week at 35 to 40°C, and then for one week at 2 to 4°C. The sample unit is then evaluated for clarity or haziness, for precipitation, and for good odorous stability when compared with a freshly prepared standard in glass. The darker-colored fragrance products seem to be more prone to precipitation.

When fragrance products are packaged in small aluminum cans, the cans should be lined with an epon-phenolic or similar material. Otherwise, the bare aluminum metal may have a reducing effect on aldehydes and certain other sensitive perfume ingredients. Some perfume components are known to cause or enhance corrosion reactions, especially the citrus types, such as bergamots and citronellal bases. Test packing is essential. Formulations that contain water are especially critical.

HOUSEHOLD PRODUCTS

General Comments

The "household products" segment of the U.S. aerosol industry reached a total of 1,424,100,000 units in 1988, accounting for 48.8% of the aerosol industry total and making this the largest category. See Table 20 for details. In Japan, the same segment amounted to 123,554,000 units in 1988, amounting to only 25.5% of the industry total. In that country, the largest market share of aerosols (44.3%) is held by personal care products.

In the U.S., the term "household products" includes all consumer aerosols except for pesticides, personal care items, and foods and drugs. They are administered by the Consumer Product Safety Commission (CPSC), which is a federal agency created in 1972 to handle the Federal Hazardous Substances Act of 1960, the Poison Prevention Packaging Act of 1970, and other laws. Among other things, they recommend pre-market testing of aerosols for flammability, inhalation toxicology, skin and eye toxicology, ingestion toxicology, and

TABLE 20. HOUSEHOLD AEROSOL PRODUCTS SOLD IN THE U.S. DURING 1988

Product Type	Number of Units	% of Total
Paints, primers, and varnishes	306,300,000	10.5
Paint strippers, "snow," decoratives	24,500,000	0.8
Room deodorants and disinfectants	181,200,000	6.2
Cleaners (glass, oven, rug, tile)	167,200,000	5.8
Laundry products (starch, pre-wash)	146,000,000	5.0
Waxes and polishes	129,100,000	4.4
Other (shoe polishes, anti-static spray)	26,800,000	0.9
Refrigerant & air/conditioner refills	90,700,000	3.1
Windshield & lock de-icers	5,700,000	0.2
Cleaners (automotive upholstery)	16,300,000	0.6
Engine degreasers	27,000,000	0.9
Lubricants and silicones[a]	92,900,000	3.2
Spray undercoatings	15,700,000	0.5
Tier inflator & sealants	34,400,000	1.2
Carburetor & choke cleaners	57,100,000	2.0
Brake cleaners	29,700,000	1.0
Engine starting fluid	30,900,000	1.1
Other automotives & industrials	42,600,000	1.5
	1,424,100,000	48.9[b]

[a]Penetrating oils, demoisturizers, rust-proofers, mold release agents, tablet machine lubricants, etc.
[b]The U.S. 1987 figures were 1,326,000,000 and 48.7%.

Note: During 1988, household aerosol products increased by 7.4% in unit volume, compared with a 6.8% growth of the aerosol industry as a whole.

(sometimes) dermal corrosivity. Additional clinical studies may be needed in some cases. If the studies are not run, or if the overall results are not placed on the label in a prescribed format, the agency will impose severe sanctions on marketers whose products are found to be injurious to consumers. In addition, any torts (lawsuits) will be much more readily prosecuted by plaintiffs against marketers whose product labels are found to not meet federal standards.

As with all U.S. aerosol products, the primary content declaration must be in units of weight (Avoirdupois ounces and pounds), although a volume or weight subsidiary declaration in the metric system is acceptable. The size of various signal words, statements of hazard, precautions, directions, weight declaration and other informational statements is controlled by CPSC regulations.

Most household aerosol products consist of a dispersion of solids or liquids in a continuous liquid phase. For paints, a group of finely divided pigments is suspended in a resin/solvent/propellant solution. For starches and fabric finishes, as well as cleaners, a colloidal suspension or emulsion of various organic materials is prepared in an aqueous solution. These products are dispensed in various ways, as shown in Table 21.

Water-out emulsions are used for most cleaners, but oil-out types are used for air fresheners, the foam-type charcoal lighters with approximately 5% water, and certain other products. The choice of propellants is very broad. In addition to all the propellants described above, isopentane (boiling point = 29.8°C), helium, oxygen, and even 0.2μ filtered compressed air have been used for a few specialty items. In the U.S., CFC propellants may be legally used for the product types shown in Table 4. Sweden, Norway, and Austria, for example, have much shorter lists of exempted or excluded products, while most other countries currently have either a production/importation restriction, or no limitations at all.

In contrast with personal care products, pesticides, and most others, household products often have very low quantities of propellant in the

TABLE 21. HOUSEHOLD AEROSOL PRODUCT DELIVERY MODES

Product	Delivery Mode
Air Fresheners	Spray
Hard Surface Cleaners	Foaming Spray
Foam-Type Charcoal Lighters	Foam
Lubricants; Decorative Strings	Stream
Boat Horns; Electronic Cleaners	Gas
Silica-based Absorbent Powders	Liquid/Solid Spray
Caulking Compounds	Paste
Lithium Stearate Grease	Gel
Talc-based Lubricants; Wind Direction Indicators for Golfers	Powder

formulas. For example, window cleaners often have 3 to 4%, starches may have 5 to 6%, certain heavy-duty cleaners may have 6 to 8%, and rug or upholstery shampoos usually carry 8 to 10 percent. The minimum amount is determined by the following factors:

- Gassing machine accuracy;
- Propellant seepage out of the dispenser during its shelf life;
- Propellant separation from the product during use, going into the expanding head space to try and maintain pressure;
- Propellant discharge during use, because of its slight solubility or entrainment in the concentrate; and
- Consumer misuse, causing momentary release of propellant phase through the valve.

Perhaps the lowest level of hydrocarbon propellant was 1.8% n.butane, used for a low-foaming window cleaner. After several years, the pressure and use level were increased. As a general rule, the amount of nitrogen or compressed air that can be pressure-filled into an aerosol can is about 1 gram per 100 mL of capacity. At levels much above this, the pressure becomes excessive.

Household aerosol products have a greater history of consumer complaints than do other aerosols. This is because they have longer shelf and service lives, often contain more powerful solvents, are stored in a greater diversity of places and conditions, and are sometimes deliberately misused. Examples of misuse are painting graffiti and the deliberate concentration and inhalation of paint vapors and other aerosols as well. In the U.S., the "Extremely Flammable" label seems to be limited to household aerosols.

The conditions of use have a profound effect on the degree of flammable hazard to the consumer or his property. Paints should only be used where adequate ventilation is available. A concrete block moisture sealer was banned by CPSC in 1974 because it was 100% flammable in composition and two to three large cans were used at a time for basement waterproofing purposes. Several lives were lost, and over a dozen houses burned down.

A fabric protectant product, designed to spray a fluoroacrylic oil and water resistant film onto entire upholstered sofas and chairs, could not have been responsibly marketed in flammable form (using acetone or ethanol as the solvent, for example). This product has the following formula:

UPHOLSTERED FURNITURE STAIN-GUARD SPRAY

3%	Fluoroacrylic or other stain-repellant active ingredient
1%	n.Butyl Acetate (Extender)
91%	1,1,1-Trichloroethane - Inhibited
5%	Carbon Dioxide

Since 96% of this formula is nonflammable, it has enjoyed great success in an important niche area; however, it has an Ozone Depletion Potential (ODP) of about 0.15. (The ODP is a relative index of ozone destruction efficiency; the value reflects the atmospheric lifetime and the chlorine content of the molecule.)

Household products have pressures that vary from about 2 to 8 bar at 21.1°C, which is the equivalent of 6.7 to 12.7 bar at 54.4°C. Those formulas that have the higher pressures often use nitrogen, nitrous oxide, or carbon dioxide as the propellant and are designed for use at very low temperatures (such as -10°C). Applications include windshield de-icing, engine starting, and dispensing a non-slip surface on ice for cars stuck in snow or ice. These gases will still retain about half their room-temperature pressure when the dispenser is chilled to -10°C, whereas most of the other propellants will sink down to such low pressures that the products become essentially unusable.

Window Cleaners

The window cleaner, developed in 1954, was the first of a large array of water-based cleaning sprays, such as hard surface cleaners, whitewall tire cleaners, oven cleaners, bathroom (basin, tub, and tile) cleaners, and laundry cleaners for spot application to difficult stains on textiles before general cleaning in the washtub or washing machine.

Window cleaner products are water solutions with from 5 to 12% hydroxylic solvents, to which a very small amount of detergent is added. Iso-propanol (C_3H_7OH) is nearly always used because it is a good grease solvent and its odor is associated with cleanliness. Additional odorants are optional. Some marketers prefer to add ammonium hydroxide (NH_4OH) in concentrations of up to 0.3% of the commercial 29% solutions of ammonia (NH_3) in water. The ammonia actually does little cleaning, but consumers associate its odor with cleanliness. Sometimes a minor amount of fragrance may be included. Oily materials and excess amounts of detergent must be avoided, or a film may be left on the glass surface, giving a halo effect in some situations. The percentage of propellant in the formula is usually 3.2 to 5.0% isobutane.

The organic grease-cutting solvents may include butoxyethanol (C_4H_9O-CH_2OH), isopropanol (C_3H_7OH), propylene glycol monomethyl ether [$HOCH_2$-$C(CH_3)H$-OCH_3), and propylene glycol monobutyl ether [$HOCH_2$-$C(CH_3)H$-OC_4H_9]. The ratio is about two parts of isopropanol (C_3H_7OH) to one part of one or two of the solvents. The detergent selection is more critical to success.

Apart from the detergent benefit, a certain amount of foam structure is needed to show where the product has been applied and also to prevent dripping from vertical surfaces. If the foam is too voluminous or stable, the wiping cloth will simply push it around, without removing it by absorption. Also, too little detergent will reduce cleaning action, while too much will cause streaking on the cleaned glass surface. Some typical window cleaner formulations are shown in Table 22 and two specialized glass cleaner formulations are shown in Table 23.

TABLE 22. WINDOW CLEANER FORMULATIONS

Ingredients	Formula A (%)	Formula B (%)	Formula C (%)
Isopropanol - 99%	4.0	5.0	4.0
Propylene Glycol Monoethyl Ether	3.0	2.5	----
Butoxyethanol	----	----	2.0
Sodium Lauryl Sulfate[a]	----	0.2	----
Lauryl Di-isopropanolamide	----	0.1	0.1
Ammonium Lauryl/Myristyl Alcohol EO 3:1 Sulfate	0.2	----	0.1
Sodium Nitrite	0.1	0.2	0.1
Ammonia (29% NH_3 in Water)	0.2	0.2	0.2
Deionized Water	89.0	88.5	90.0
Isobutane A-31	3.5	3.3	3.5

[a]Such as Sipon WD, a product of the American Alcolac Corp.

TABLE 23. ANTI-FOGGING OR ANTI-STATIC GLASS CLEANER FORMULATIONS

Ingredients	Formula A (%)	Formula B (%)
Dioctylester of Sodium Sulfosuccinic Acid[a]	0.05	0.08
Silicone Glycol Copolymer[b]	0.30	0.40
Alkoxylated (8) n.nonylphenol[c]	0.10	----
Propylene Glycol Monoethyl Ether	3.52	3.49
Isopropanol - 99%	8.00	10.00
Morpholine	0.03	0.03
Deionized Water	84.00	82.00
Isobutane A-31	4.00	4.00

[a]As Aerosol OT-100, by the Chemical Product Division of the American Cyanamid Company, or Monawet MO-70E by Mona Industries, Incorporated.

[b]As Dow Corning 193 Surfactant, by the Dow-Corning Corporation. Water-soluble, gives gloss, non-tackiness, anti-fog, surface tension depression, and anti-static properties.

[c]As Triton W-30 by the Rohm & Haas Company, gives added grease removal and cleaning power.

The products in Table 22 are used mainly for windows, but they can also be employed to clean refrigerators, stove tops, kitchen counter tops and other hard-enameled, painted, or chinaware surfaces. Because of their special properties and somewhat higher cost, the aerosols in Table 23 are used more for bathroom mirrors (to prevent steaming), where anti-static properties are desired, and where a relatively glossy, polished appearance of the glass surface is desired. One version of this type of product is eyeglass lens cleaner, with dispensers in the 15-gram size that use metered spray valves delivering approximately 50 microliters per actuation. These products give about 300 actuations. Despite a general preference for the small sizes, containers holding as much as 460 grams of "Lens Cleaner - Antifog" are on the market.

Spray Starch

The self-pressurized starch was developed around 1958 and used about 4% of highly refined corn starch as the essential ingredient. Some of these starches can be dispersed into the aqueous phase at temperatures as low as 30 to 35°C, but others may require pre-cooking a 20% starch/borax (Sodium Tetraborate 10-Hydrate; $Na_2B_4O_7 \cdot 10H_2O$) with live steam at 4 bars and 150°C. The resulting thin paste, now concentrated to 18% solids as the result of some condensation of the steam, drops into the batch-making tank containing agitated water and is quickly dispersed. The other ingredients are then added, after which the pH is adjusted to about 8.2 at 25°C.

Starch dispersions have been corrosive to cans, but if ingredients with a low chloride content are selected, and sometimes if a modest amount of corrosion inhibitor is added, a single-lined can is sufficient for a two- or three-year shelf life. One starch formula that uses 0.04% sodium benzoate inhibitor has been successfully marketed in a plain 4.48 g/m^2 (0.20 lb/ft^2) container. If the starch contains a significant amount of chloride ion corrosion promoter left over from sodium hypochlorite (NaClO) bleaching operations, corrosion can become a significant problem and a double-lined can must be used, along with 0.20% sodium nitrite or similar inhibitors. Three typical starch formulations are shown in Table 24.

TABLE 24. SPRAY STARCH FORMULATIONS

Ingredients	Formula A (%)	Formula B (%)	Formula C (%)
Amizo No. 513 Pearl Starch	2.30	----	----
Penford Gum 290 or Equivalent	----	2.75	----
EO-Size 5795 Starch or Equivalent	----	----	3.00
Sodium Tetraborate 10-Hydrate	0.30	0.40	0.45
Silicone emulsion LE-463, 346 or equal. (60% Active Ingredient)	0.40	0.50	0.45
Silicone antifoam emulsion, as SAG-470 by Union Carbide	0.15	0.10	0.10
Sodium Nitrite or Sodium Benzoate	0.15	----	0.10
Fragrance	0.02	0.03	0.03
Glutaraldehyde (50%) or Formaldehyde (37% in Water)	0.04	0.05	0.03
Optical Brightener; as Tinopal 4BM	0.02	----	----
Deionized Water	91.20	91.70	90.00
Isobutane A-31	5.50	6.00	5.84

Note: Adjust pH to 8.4 ± 0.2 at 25°C, using triethanolamine (99%) or a 10% solution of sodium hydroxide.

The optical brightener ingredient is now rarely seen. It adds cost and has only slight marketing appeal.

If available, glutaraldehyde is preferred over formaldehyde, since the latter is less effective as a microbicide and may be a low-order carcinogen. Glutaraldehyde is marketed by Union Carbide Corporation.

The sodium tetraborate, added as the 5- or 10-hydrate, combines chemically with the starch to give it better properties, such as less buildup on the sole plate of the iron, and also functions as a corrosion inhibitor. The silicone emulsions increase the easy slip of the iron over the cloth, so that the user has less fatigue and almost no wrinkling or bunch-up problems. The starch foam should quickly absorb into the textile, and should not be pushed around by the iron. If this is not the case, either a 10% or 100% silicone anti-foamant is added. This ingredient consists of a silicone oil that contains billions of tiny sharp splinters of silica (SiO_2). The silica acts to puncture the foam bubbles so that they quickly collapse. Antifoams are used in about half of all starch products.

Since starch solutions are nutrients for bacteria, yeasts, molds, fungi, and rickettsia, it is necessary to perform the following steps during production:

- Pasteurize the deionized water, or filter it at 0.2μ to remove microorganisms. (Resistant strains of pseudomonads are hard to kill chemically, but they are eliminated by heating for one minute at 40°C or higher.)

- Sanitize the batch-making tank, the concentrate filler, and all the pumps, filters, piping, and other equipment.

- Do not hold the starch concentrate for more than 72 hours, and then only in covered tanks.

- Flush the deionizer beds periodically with a strong formaldehyde solution, to prevent the proliferation of microorganisms on the resins.

Some fillers also run a Total Plate Count (TPC) study on starch batches and finished aerosols. Since these tests require 48 hours for a reliable result, the batch will normally be packed into cans and corrective action will be severely limited. The best result will indicate that there are "fewer than

10 microorganisms per cubic centimeter of product." Therefore, the possibility of proliferation still exists. Experience with starches, fabric finishes, mousse products, and others that can support microbial growth suggests that the possibility of growth is low once the aerosol can has been packed. For example, non-facultative aerobic bacteria generally die from lack of oxygen. In the rare instances of starch contamination, bacteria have caused "ropiness," or little tendrils of retrograded material in the product, leading to valve problems and odors from triethylamine and other substances.

Most starch formulas use 0.03 to 0.035% Formalin (37% formaldehyde, HCHO, in water). Sodium o.phenylphenate is still occasionally used. However, a preferred material is glutaraldehyde [$CH_2(CH_2{\bullet}CHO)_2$]. This material has very broad spectrum activity, is low in cost, effective at concentrations even lower than formaldehyde, and does not sometimes sting the nose of the user during the ironing process.

A significant amount of work has gone into refining the designs of valves that will be best for starches. The best spray pattern, for instance, is a "doughnut" or torus shape, without "hot spots" or areas of extra-heavy product concentration. This pattern gives the most uniform spray density as the spray is sprayed across the fabric.

Most starches in the U.S. now use either vertical-acting or toggle-type valves whose button and stem are separate components. In general, the buttons are of the two-piece type, with a plastic insert of 0.46 to 0.50 mm orifice design. However, a new "pseudo-mechanical breakup" one-piece button by the Precision Valve Corporation is now being used commercially.

During product development, valve candidates are tested against production or commercial control units for the incidence of valve problems. The test often involves 72 dispensers and lasts two weeks. The caps are left off to enhance product evaporation at the valve.

Protocols differ, but one starts on a Monday, with 48 cans being sprayed for 5 to 10 seconds on the following schedule: 2, 2, 3, 2, 2, and 3 days, and

24 cans being sprayed every seven days. The results are recorded in the following ways:

- Clear (Normal);
- Streams--three seconds or less--then clears;
- Streams--sustained streamer--over three seconds; and
- Plugger.

If more than two sustained streamers or one plugger are encountered, the valve or formula should be adjusted to be more reliable. If the control, using a different valve, gave acceptable results, this suggests that the experimental valve needs improvement, not the formula.

Starch products work better on cottons and on 50% cotton and 50% polyester fabrics than on textiles of higher polyester content, i.e., the so-called "synthetics." Some marketers have developed Fabric Sizing or Fabric Finish aerosols especially for these synthetics. As the market for synthetics diminished during the last 10 years or so, consumers began to discover that they liked the performance of these fabric finishes on straight cottons and high-cotton blends. They did not have the relative stiffness of the starches, but gave the fabrics lubricity, a better feel or handle, and an impression of heaviness and brighter colors, making them seem more like new garments. since the product was based on sodium methylcellulose gums, the Fabric Finish produced a somewhat higher-quality spray and had a higher-quality image than the starch. It is a useful supplementary product, and sales were estimated to be about 12 to 14% of the starch market in the U.S. in 1988. Table 25 presents a formulation for aerosol fabric finish.

Heavy-Duty Hard-Surface Cleaners

This product was an outgrowth of the window cleaners. It is sold in two versions: one with a microbicide, and the other without such an ingredient. If the cleaner has a microbicide and is labeled accordingly, in the U.S. it falls under the jurisdiction of the Environmental Protection Agency (EPA)

TABLE 25. FABRIC FINISH FORMULATIONS

INGREDIENTS	FORMULA (%)
Sodium Methyl Cellulose (Combination of low and medium-low viscosity products). Technical Grade preferred.	0.9
Polyethylene Glycol (Mol.Wt. 400)	0.9
Coco-β-amino-propionic Acid (60% in water)[a]	0.02
Dimethylsilicone Emulsion (60% in water)	0.3
Silicone Anti-foam (100%)	0.03
Ammonium Hydroxide (29% NH_3 in water)[b]	0.02
Glutaraldehyde (50% in water)	0.03
Sodium Nitrite	0.05
Fragrance	0.05
Deionized Water	92.70
Isobutane (A-31)	5.00

[a]Deriphat 151, by Henkel Corporation.

[b]Used to neutralize the Deriphat 151 (Acid) and adjust the pH value to 8.6 $\pm$ 0.2 at 25°C.

FIFRA and is subject to a heavy burden of microbiological testing, label review, and confidential formula disclosure before marketing. The delay period is currently one to two years, and an annual registration fee must also be paid to EPA and to state agencies. Some marketers elect to include microbicides in their products and sell them without making any claims, since the cost differential is extremely small.

The first hard-surface cleaner was introduced around 1961. The products are characterized by a combination of non-ionic and tetrasodium ethylenediaminetetraacetate (Na_4EDTA) detergents, plus various alcohol- or glycol-based solvents in a water base. Two typical hard-surface cleaners are shown in Table 26.

The tetrasodium EDTA, present at 1.90% (Formula A) and 1.52% (Formula B) is effective at removing calcium carbonate, which it does by a sequestering action, producing soluble calcium ethylenediaminetetraacetate [$Ca_2(EDTA)$]. The dissolution process is a slow one if the lime has any significant thickness; therefore, the main thrust is one of preventive maintenance. Rust deposits are similarly dissolved. These uses suggest various bathroom applications.

Higher pH versions, sometimes with 25% deodorized kerosenes added, have been used as whitewall tire cleaners. Anhydrous versions, generally containing about 5% non-ionic surfactant, 20% xylenes, 72% deodorized kerosene, and 3% carbon dioxide are used for cleaning the exterior of car engines. After use, the cleaner can be flushed away with tap water. It is generally advisable to perform the cleaning operation outside on a cool engine that is not running. Hydrocarbon propellants, such as propane (A-108), have been used for these products, but they are not recommended because of their flammability.

A second anhydrous version, in this case not containing any surfactant materials, is carburetor and choke cleaner. It typically contains 60% toluene or (better) xylenes, 30% diacetone alcohol or acetone, and 10% propane. It is obviously extremely flammable, and should be used in small amounts and with care in an open and well-ventilated area. The engine should be cool and

TABLE 26. HARD SURFACE CLEANER FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)
Atlas G-3821 Detergent	-	0.50
Tergitol 15-S-9 (Non-ionic surfactant)	0.50	-
Tetrasodium EDTA (38% in water)[a]	5.00	4.00
Triethanolamine - 85%	-	1.00
Propylene Glycol Monobutyl Ether	5.00	6.00
Sodium Meta-Silicate 5-Hydrate	0.10	-
Sodium Sesqui-Carbonate	-	0.10
Morpholine	0.20	0.15
Ammonium Hydroxide (29% NH_3 in Water)	-	1.00
Sodium Hydroxide (50%) or Citric Acid (50%)[b]	q.s.[c]	q.s.[c]
Fragrance	0.10	0.15
Deionized Water	82.10	79.90
Isobutane (A-31)	7.00	7.20

[a]Although a specific surfactant was mentioned, any one or more of the following may be used:

- Linear primary alcohol polyglycol ether (9 to 12 mol ethylene glycol (ETO); average);
- Linear secondary alcohol polyglycol ether (9 to 12 mol ETO; average); or
- Nonylphenol polyoxyethylene (9 to 13 mol ETO; average).

[b] These reagents are used to adjust pH value to 10.5 ± 0.2 at 25°C.

[c] Quantum sufficit (a sufficient quantity).

turned off. Any excess should be removed before the car is restarted. The use of a nonflammable propellant, such as HCFC-22 or carbon dioxide, would act to make the overall product only slightly less flammable.

The final version of a hard-surface cleaner is oven cleaner. There are both caustic formulas and "pre-caustic" formulas. The caustic ones use from 4 to 8% sodium hydroxide activated by triethanolamine to cut through the varnish-like deposits of grease and food spatters on oven surfaces. The other form contains alkali metal acetates and sometimes other organic salts in a water and surfactant slurry. The product is sprayed on the oven surfaces, after which the oven is closed and heated. This causes the organic salts to pyrolyse via a distinctly two-stage process, producing the oxide, carbon dioxide, and water. The oxide then hydrates to the hydroxide form, which begins dissolving the baked-on greases and other residues. Table 27 presents the formulations of oven cleaners.

The caustic nature of Formula A in Table 27 allows it to rapidly corrode aluminum surfaces, and this is often mentioned on labels. Under U.S. regulations, if an oven cleaner contains more than 2% of a caustic such as sodium hydroxide, the dispenser must be fitted with a child-resistant closure. The same regulations permit one exempt package size designed for homes without children and for adults with physical problems like arthritis who would otherwise have great difficulty using the product. In practice, the marketplace has shown a strong preference for the products without the special closures, so that dispensers that have this feature are now only a token part of the overall sales picture. Self-cleaning ovens in the U.S., Europe, and other areas will reduce sales of aerosol oven cleaners.

The other type of heavy-duty cleaner is designed for the specialty cleaning of textiles. The best known is the pre-laundry cleaner stain remover, which is sprayed directly onto a stain and onto the inner neck band of shirts, shirt cuffs, and other areas where dirt and grime seem to concentrate. After spraying, the garment may then be laundered. Some formulations contain enzymes for the more effective removal of proteinaceous stains; e.g., grass stains or bloodstains. Others use a mild detergent system and claim

TABLE 27. OVEN CLEANER FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)
Potassium Formate	-	6.0
Potassium Acetate	-	6.0
Sodium Hydroxide	5.0	-
Calcium Dodecylbenzene Sulfonate	-	3.0
Compatible Thickener	-	0.5
Sodium Nitrite	0.2	0.2
Triethanolamine - 99%	1.0	-
Tetrasodium EDTA - 38%	1.0	-
Deionized Water	87.8	78.3
Isobutane (A-31)	5.0	6.0

that the treated garments may be stored for several days before washing, if so desired.

The two major formula types are anhydrous and water-based. The latter generally contains 25 to 40% water. Originally, soil removal was accomplished by using 20 to 25% perchloroethylene, in addition to the usual anionic/nonionic detergent system and hydroxylic solvents. The perchloroethylene ($Cl_2C{=}CCl_2$) was a major benefit to the cleaning activity, doing such a good job, in fact, that many users complained that their clothes were cleaner and whiter where the product was applied than in the other areas. Some wondered if the product contained a bleaching agent. The marketers maintained a service for taking care of shirts and other garments submitted to them by consumers for correction or replacement, and what they normally did was to immerse the entire item in the concentrate for a few minutes, rinse it off, dry the garment and return it. The super-cleaning ability of the aerosol product had removed soils that resisted ordinary cleaning methods and that had built up on the garment over months of use, turning the cloth slightly grey or slightly tan. Eventually, the perchloroethylene was deleted, after the Bruce Ames "mutated Salmonella" test suggested that it might be a carcinogen and after a number of more odor-conscious consumers complained that traces of the chlorocarbon odor could be detected in clothes even after they were automatically washed, dried, and ironed. The two main formula types of textile cleaners are illustrated in Table 28.

The isopropanol functions as a mild cleaner, but (just as importantly) as a foam destabilizer and suppressant. Ethanol may also be used for this purpose. In either case, percentages may vary according to the foaming tendencies of the overall formula.

Carpet and Rug Cleaner

This unique product was introduced around 1964 by S. C. Johnson & Son, Inc. It is presented in a very large can, such as the 75x192 mm (USA: 300x709) or the new, necked-in 72x261 mm (USA: 211-213/214x1005), which have

TABLE 28. PRE-LAUNDRY CLEANER FORMULATIONS

INGREDIENTS	FORMULA A	FORMULA B
Linear primary or secondary alcohol polyglycol ether [2 to 4 mol ethylene glycol (ETO)]	12.0	-
Linear primary or secondary alcohol polyglycol ether (7 to 10 mol ETO)[a]	12.0	10.0
Diethylene Glycol Monomethyl Ether	12.0	5.0
Sodium Laurate/Myristate	0.4	-
Isopropanol - 99%	4.0	5.0
Low-odor n.Paraffinic or iso.Paraffinic Solvent (C_{10} - C_{14} Hydrocarbons)	20.0	786.7
Ammonium Hydroxide (28% NH_3 in Water)	0.5	-
Fragrance (Typically lemon/lime)	0.5	0.5
Enzyme Concentrate (Optional)	1.0	-
Deionized Water	30.1	-
Propane A-108 or Propellants A-85	7.5	-
Carbon Dioxide	-	2.8

[a]May be replaced with octyl or nonyl phenol polyoxyethylene (9 to 13 mol ETO) or other non-ionics of similar HLB value.

capacities of about 820 and 980 mL, respectively. This allows one can to clean a carpet of maximum area.

The products use sodium lauryl sulfate, which acts to pull the dirt and grime out of the carpet fibers and then dries so that vacuum-cleaning can effectively remove it. An emulsified polymer is included to prevent rapid re-soiling of the absorbent fibers. Table 29 gives a typical carpet cleaning formula.

Intensive wetting of the warp and woof of the carpet is not desired, as would occur if sodium stearate/palmitate soaps were to be used. Excessive wetting lengthens drying time, and might also cause mold formations at the base of the carpet or rug. The sodium/magnesium lauryl sulfate combination wets only the surface of the fibers, where most of the dirt is collected. In particular, the magnesium lauryl sulfate helps surround the dislodged dirt into a more friable, dried mass on the surface of the fibers, for easy removal with a vacuum cleaner.

The sodium lauryl sarcosinate functions as a corrosion inhibitor, more or less specific to lauryl sulfate ion and ethoxylated or propoxylated lauryl sulfate moieties. However, for it to function well, there must be a virtual absence of chloride ion, bromide ion, and copper ion. The highly purified "toothpaste" grade of sodium lauryl sulfate (SLS) is acetone extracted or otherwise treated to remove any chloride ion that may be present, depending on the method of synthesis used. Sodium nitrite has often been added to these formulas as an additional corrosion inhibitor.

The upholstery shampoo is a related aerosol product that uses such detergents as sodium lauryl sulfate or morpholinium stearate, plus ingredients such as lauryl-monoethanolamide as a corrosion inhibitor and foam stabilizer. The foam is worked into the upholstery covering with a rough cloth or soft-bristle brush, then allowed to dry before removal. A water-wipe is often used to remove the last bits of product, so that a slightly soapy feeling will not be noticed.

TABLE 29. RUG AND CARPET CLEANER PRODUCT FORMULATION

INGREDIENTS	FORMULA (%)
Sodium Lauryl Sulfate (very low in Chloride Ion)[a]	1.60
Magnesium Lauryl Sulfate (very low in Chloride Ion)[b]	1.20
Sodium Lauryl Sarkosinate - (30% in Water)[c]	3.00
Styrene Maleic Anhydride Copolymer - (15% in Water)	20.00
Optical Brightener; as Calcofluor SD (Optional)	0.02
Ammonium Hydroxide (28% NH_3 in Water)[d]	0.16
Fragrance	0.08
Deionized Water	66.44
Isobutane A-31	7.50

[a]As Maprofix 563, by the Onyx Division of Witco Chemical Co.

[b]As Maprofix Mg.

[c]As Maprosil 30.

[d]Used to adjust the pH value to 9.8 $\pm$ 0.2 at 25°C, although up to about 1.5% may be used if the clean odor of ammonia (NH_3) is desired.

Silica-Based Absorbent Fabric Cleaners

A relatively unique aerosol product uses the extreme absorbency of very finely divided silica powder to literally soak up stains by capillary action. Silica, which has been made by the pyrolysis of silicon tetrachloride, is able to absorb hundreds of times its own weight of various liquids, even greases and gels, and this principle is used here. The silica, in the form of an essentially nonflammable slurry in 1,1,1-trichloroethane, is sprayed onto the fabric to be treated. The solvent quickly evaporates, causing the silica powder to absorb any available liquid materials. After complete drying, the loaded silica is brushed off the cleaned fabric, using light strokes, so as not to embed it in the fiber matrix. The aerosol dispenser often comes with a special plastic cap whose top is molded to have 100 to 200 thin, comb-like tines or bristles. The cap is used to brush off the silica.

A typical formulation follows:

ABSORBENT SILICA CLEANER FORMULATIONS

Ingredients	Formula (%)
Fumed Silica Powder	6.00
1,1,1-Trichloroethane	68.00
Isopropanol - 99%	10.00
Fragrance	0.05
Propane A-108	15.95

The selection of silica powder and a valve with optimum design features are keys to success, since with an incorrect combination, valve plugging may occur. The user can correct this problem only 40 to 60% of the time. There are also considerable problems with evaporation, concentrate losses, toxicological response to 1,1,1-trichloroethane vapors (unless used in a well-ventilated room) and weight control in the manufacture of these products, so that one should not undertake their manufacture lightly.

These cans, when actuated under totally non-conductive conditions, will build up a static charge in the 67,000 to 285,000 V range, based on the results of one fairly large study. This does not adversely affect the consumer in any way, but if a filled can is jammed, defective, or otherwise quickly discharges the contents in a gas house while momentarily not grounded, the spark to a nearby grounded surface may cause ignition of the discharge plume, perhaps with serious consequences. No viable corrective methods for this phenomenon have yet been devised.

Air Fresheners

The air freshener was the second aerosol product to be developed commercially, after insecticides. It was marketed in the U.S. as early as 1948, mainly by oil companies, and then by chemical specialties marketers such as the Colgate-Palmolive Company. The formulas were initially combinations of 1% fragrance, 15% low-odor petroleum distillate, and 84% CFC-12/11 (55:45), until about 1961, when the S. C. Johnson & Son, Inc. firm began to market their line of "Glade" Air Fresheners in a water-based form. These formulations now make up the largest segment of this category. The remaining segments are the "super-dry" sprays, typically containing 99% propellants, and the alcoholic types that average about 50% ethanol. Typical examples of the three versions are presented in Table 30. The use of dimethyl ether propellant in Formula B is justified by the increased solvency of perfume resins that might otherwise precipitate.

As mentioned earlier, Formulas B and C have a Volatile Organic Compound (VOC) level of essentially 100 percent. After February 28, 1990, the State of New Jersey (U.S.) has forbidden the marketing of these formulas unless the VOC content is somehow reduced to 50% or less. The use of 1,1,1-trichloroethane (not a VOC, though it has a potential for stratospheric ozone depletion) is not permitted. Ultimately, it may be necessary to use a combination of something like 6 parts water and 44 parts HFC-152a (replacing 50 parts of Propellant Blend A-60) to be in compliance with the regulations. This change will have a major effect on the retail cost of these products.

TABLE 30. AIR FRESHENER FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)	FORMULA C (%)
Fragrance	1.00	1.50	2.00
Odorless Petroleum Distillates	6.28	-	6.00
Lanpolamide 5 Liquid (Croda, Inc.) PEG Lanolinamide and PEG Lanolate ester - 50% in Deodorized Kerosene (HLB = 3.65)	0.72	-	-
S.D. Alcohol 40-2 (Anhydrous)[a]	-	-	38.00
Sodium Benzoate	0.15	-	-
Deionized Water	59.85	-	4.00
Propellant Blend A-60[b]	32.00	90.00	50.00
Dimethyl Ether	-	8.50	-

[a]Specially Denatured ethanol, where 400 g of tertiary butanol [$(CH_3)_3COH$] and 42 g of brucine sulfate are added to every 3,600 liters of anhydrous ethanol.

[b]Contains typically 62 weight percent isobutane, 2 weight percent of n.butane, and 40 weight percent of propane.

Disinfectant/Deodorant Sprays

This category has often been compared with air fresheners, but there are more differences than similarities. First, the "D/D" products are regulated by the U.S. EPA, so that planning and formula development should be carried out at least three years before the marketing phase begins. Secondly, most of the label is given to a description of the formula, disinfectant claims, and directions for disinfecting hard surfaces. The ability of the product to function as a space spray is limited by the low levels of propellant used, since the main use is as a surface spray, and labeled uses limit space spraying to storage rooms, closets, and other enclosed spaces for deodorizing purposes only. (Fragrance benefits are not mentioned on the label, although a pleasant fragrance is always included, even in "Hospital Strength" D/D products.)

Two formulation types and two propellant types are currently in use. The base product contains either an o.phenyl-phenol system or a quaternary ammonium disinfectant system in a hydro-alcoholic solution. Either 5% carbon dioxide or about 20% hydrocarbon propellant blend is used as the pressurizing medium. In terms of units sold, the o.phenyl-phenol and carbon dioxide system is probably the most popular.

The EPA requires that the labels of these products list the active ingredients, plus certain other data. An example from the label of one such product is shown below:

Active Ingredients:
- n-Alkyl (60% C_{14}, 30% C_{16}, 5% C_{12}, 5% C_{18}) dimethyl benzyl ammonium chlorides 0.072%
- n-Alkyl (68% C_{12}, 32% C_{14}) dimethyl ethylbenzyl ammonium chlorides 0.072%
- Ethanol 53.088%
- n-Alkyl (92% C_{18}, 8% C_{16}) n-ethyl morpholinium ethyl sulfate 0.040%

Inert Ingredients:
46.728%
Contains sodium nitrite

The first two ingredients are available as BTC 2125M, which is sold as a 50% active ingredients solution (and in other strengths) by the Onyx Division of the Witco Chemical Company. Similarly, the last n-Alkyl compound is sold as Atlas G-271, generally as a 35% active ingredient solution, by ICI America, Inc. Two examples of these formulas are provided in Table 31.

The quaternary ammonium chloride products came along well after the market for D/D aerosols was well established and approaching 100,000,000 units sold a year in the U.S. The strengths and weaknesses of their antimicrobial spectrum of efficacy is different from that of o.phenyl-phenol and its close derivatives, as would be expected. Also, since the quaternaries are much less volatile than the substituted phenols, the protective effects may last longer. This may be important when considering regrowth potential for molds in leather, wood, books, and other relatively porous substrates. No one has attempted to market a product containing both microbial types, perhaps because of the degree of toxicological and microbiological testing that would be required.

Since they have chloride ion (a strong corrosion promoter) double-lined cans and heavy amounts of strong corrosion inhibitors have been required to achieve an adequate shelf life for the quaternary ammonium formulations. For some time, combinations of sodium nitrite and morpholine were preferred for the inhibitor system, but after it was found that up to about 10 parts per million of morpholinium-N-nitrosamine (a carcinogen) could be formed in situ over one year of room-temperature storage, marketers acted to change the sodium nitrite to sodium benzoate and eliminate the reaction.

Disinfectant Cleaners

This type of product was partially covered under "Hard Surface Cleaners" (see Table 26), but the disinfectant version adds a new dimension of cleaning that is generally appreciated by the consumer. Most of the larger marketers of heavy-duty cleaners are able to cope with EPA's requirements for pre-marketing registration, plus federal and state fees, and have preferred this type of presentation. The disinfectant cleaner is really nothing more than

TABLE 31. DISINFECTANT/DEODORANT FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)
o.Phenyl-phenol (98% purity)	0.110	-
BTC-2125M (50% in water)[a]	-	0.288
Atlas G-271 (35% in water)[a]	-	0.114
S.D. Alcohol 40-2 (Anhydrous)[b]	73.380	52.068
Fragrance	0.110	0.110
Sodium Benzoate	0.200	0.220
Morpholine	0.200	0.200
Deionized Water	21.000	25.000
Propellant Blend A-40[c]	-	22.000
Carbon Dioxide	5.000	-

[a]For chemical compositions, see preceding page.

[b]For chemical composition, see note 'a' of Table 30.

[c]10 wt % propane and 90 wt % isobutane.

the standard type, except for the inclusion of 0.20% or so of biocidal material in the formula. When a quaternary microbicide is used, the formula has to be adjusted to eliminate incompatible anionic surfactants that might precipitate the active cationic moiety. Some remain acceptable, as will be seen in the formulation presented in Table 32.

Normally, two types of valves are used for both these and the regular hard surface (basin, bath, and tile) cleaners. The can may be used in different positions, including some where the dip tube may protrude into the gas space. The simplest and least costly approach is to use a valve with a very large diameter, a "jumbo" dip tube, with an inside diameter of about 6.4 mm. For the relatively long cans in general use, such tubes will contain 7 to 8 grams of product. If the container is turned upside down--for instance, to more comfortably spray the base of a toilet bowl--the special dip tube will hold sufficient product for about 6 seconds of spray time. After this, gas will be emitted, signalling the consumer to reverse the can for a second or two. In the second approach one might use the Sequist Valve Company Model NS-36 (Ball-check) valve. A 4-mm diameter stainless steel ball travels in a short plastic slot, just below the valve. With the can upright, an orifice at the bottom of the slot is closed off, forcing the product to travel up the dip tube and through the valve. With the can inverted, the ball closes off an orifice at the opposite end of the slot. This acts to plug the opening from dip tube to valve and at the same time opens a "vapor-tap" type orifice directly into the valve chamber. The valve has only two minor deficiencies: it always leaks slightly between the plastic and the ball, to give a vapor-tap effect, and secondly, it works poorly when the can is in an essentially flat position. The price is significantly higher than that of the standard valve or jumbo dip tube valve.

A good delivery rate for the hard-surface cleaners is about 1.23 g/sec at 21°C, at the 460-mm vacuum crimp pressure of about 2.54 bar at that temperature. A valve with a 0.46-mm stem and 0.41-mm MB-ST button will provide the desired rate.

TABLE 32. DISINFECTANT CLEANER FORMULATIONS

INGREDIENTS	FORMULA (%)
Sodium Meta-Silicate 5-Hydrate	0.10
Tetrasodium EDTA (38% A.I. in Water)[a]	4.12
BTC 2125M (50% A.I. in Water)[b]	0.40
Sodium Benzoate	0.10
Sodium Tetraborate 10-Hydrate	0.10
Morpholine	0.20
Ammonium Hydroxide (As 29% NH_3 in Water)	1.10
Atlas G-3821 Non-ionic Surfactant[c]	0.50
Butyl Cellosolve (or similar)[d]	6.00
Potassium Hydroxide (45% A.I. in Water)	0.05
Fragrance	0.15
Deionized Water	80.18
Isobutane A-31	7.00

[a]Tetrasodium Ethylenediamine-tetraacetate, such as Cheelox BF-13, or Versene 30 (Dow).

[b]See previous pages for complex formula of ingredients.

[c]By ICI America, Inc.

[d]By Union Carbide Corporation. Propylene Glycol Monomethyl Ether may also be used.

Paint Products

In 1988, the U.S. paints and coatings industry marketed approximately 325,000,000 units, ranging from very small touch-up paints to large-size units for domestic or industrial furniture finishing. A substantial number of filling plants specialize in self-fill or contract filling operations. It is a complex area, with five main categories: enamels, lacquers, varnishes, stains, and primers, with subgroups of each. Large numbers of colors have also to be considered. The largest sales are for the alkyd- and acrylic-base paints. Both are available in anhydrous and water-based formulations, although the water-based techniques are better developed in some countries than others, as is the use of dimethyl ether as a paint propellant. The formulas to follow illustrate a bronze metallic specialty lacquer (anhydrous), two alkyd types and an acrylic type. The last three are based on some excellent work by DuPont that has been widely distributed. The term lacquer refers to a coating that dries by the simple evaporation of the solvent system. Originally, it related to the cellulosic varieties, but these have been almost completely displaced by the thermoplastic acrylics. The acrylics have better resistance to mild chemicals, weather, and sunshine. They are a preferred base for various metallic finishes (aluminum, bronze, and gold powder finishes) because of their low acid number and water-white color. Four different paint formulations are illustrated in Table 33.

A prototype valve that might be evaluated is the Newman-Green Model R-10-123 (0.33-mm vapor-tap), but with a butyl rubber seal gasket. The actuator is a No. 120-20-18. This valve delivers the four products shown in Table 33 at about 0.95 g/sec at 21.1°C.

During the development of various paint aerosols, alterations in the formula or valve may be required if the applied product exhibits low gloss, blushing, sagging, bubbling, peeling, deleafing of metallics, valve plugging, poor adhesion, low durability, or other problems. For example, adding more xylenes to Formula A would slow down the final drying of the film, resulting in better smoothness and higher durability. The disadvantage must be weighed against the two advantages, keeping in mind that the consumer will note the

TABLE 33. VARIOUS AEROSOL PAINT FORMULATIONS

INGREDIENTS	ACRYLIC METALLIC FORMULA A (%)	ACRYLIC FORMULA B (%)	ALKYD FORMULA C (%)	ALKYD FORMULA D (%)
Acryloid B72 (50% A.I.)	8.0	-	-	-
Acryloid A101 (40% A.I.)	1.0	-	-	-
Carboset 514H (40% A.I.)	-	25.00	-	-
Gold Powder #6238	4.0	-	-	-
Tint Ayd (Black WD-2350)	-	5.00	5.00	5.00
Beckosol 13-400 (75% A.I.)	-	-	13.00	13.00
Ammonium Hydroxide (29% NH_3)	-	-	1.15	1.15
Titanium Dioxide Powder, R-940	-	1.00	2.00	-
Propylene Glycol Monomethyl Ether	2.0	5.00	5.00	5.00
Isopropanol	-	8.00	8.00	8.00
Nonylphenoxy Polyethoxy Ethanol	0.1	0.35	0.45	0.50
Fluoroacrylic FC-430 Surfactant	-	0.02	0.02	0.02
Hi-Sil T-600 (Silica)	-	0.14	0.14	0.14
Magnesium Aluminum Silicate	-	0.30	0.12	0.15
Drier: Cobalt Hydro Cure II	-	-	0.10	-
Drier: Zirconium Hydro Cem	-	-	0.08	-
Toluene	28.2	-	-	-
Xylenes	12.4	-	-	-
Acetone	15.0	-	-	-
Deionized Water	-	10.19	19.94	22.04
Hydrocarbon Propellant Blend A-85	28.9	-	-	-
Dimethyl Ether	-	45.00	45.00	45.00
Pressure (460-mm Vacuum Crimp bars at 21.1°C.)	3.4	3.9	3.8	3.8

(Continued)

TABLE 33. (Continued)

Ingredient Sources:

Acryloids	Rohm & Haas Company
Carboset	B. F. Goodrich Company
Gold Powder	U.S. Bronze, et al.
Tint Ayd	Daniel Products Company
Beckosol	Reichhold Chemical Company
Titanium Dioxide	E. I. duPont de Nemours & Co., Inc.
Propylene Glycol MM Et	UCAR PM - Union Carbide Corporation
Nonylphenoxy Poly.	Triton N-401 - Rohm & Haas Company
Fluoroacrylic	3M Company
Hi-Sil	PPG Industries, Inc.
Magnesium A.S.	Attagel 40 - Engelhard Corporation
Driers	Mooney Chemicals, Inc.
Dimethyl Ether	Dymel A - E. I. duPont de Nemours & Co., Inc.

disadvantage rather soon after the product is used, but may not detect the other differences until later, if at all.

Paints and coatings are generally packed with a small glass marble that helps agitate settled material back into a uniform dispersion. Also, to prevent premature use by children or others, a tamper-resistant and tamper-evident valve cover or protective cap is used. The outer cap is often colored the same as the product within the can, or it may carry a self-adhesive top label to help the customer make selections.

Furniture Polishes

The original aerosol furniture polishes were introduced around 1950. They contained self-polishing floor waxes in a simple oil-in-water emulsion form. In 1955, silicone emulsions were included, since they added lubricity and made the rubbing out process much easier. They also improved the sheen and conferred water resistance to the polish. At first, formulators added an intermediate viscosity silicone, such as Dow-Corning DC-200 dimethylsilicone fluid (1,000 cstks), at a low-volatiles level about the same as that of wax: 0.7 to 1.5% of the total. But as they found that silicones soaked into the polishing cloth more readily than wax, they began to increase silicone levels. In addition, it was found that combinations of lower- and higher-viscosity silicones functioned better than the single intermediate viscosity type. The higher-viscosity silicone added shine or brilliance, but too much caused the polished surface to be subject to marking. Two illustrative examples are shown in Table 34.

The preparation of furniture polish concentrates can present fire and explosion hazards, especially if the more volatile aliphatic hydrocarbons are used, such as Isopar C, which has a flashpoint of 5°C. Heating batches of Isopar C to 80°C or so to facilitate the dissolution of waxes has caused four major explosions and subsequent fires. This is because very heavy vapors of the hydrocarbon seep over the tank rim, fall to the floor, and spread outward until a spark or fire source is contacted. Less than 1 volume percent of

TABLE 34. FURNITURE POLISH FORMULATIONS

INGREDIENTS	FORMULA A[a] (%)	FORMULA B[b] (%)
Wax S and Wax N (1:1 ratio) Hoechst	1.25	1.25
Silicone Emulsion LE-461 (50% A.I.) UCC	1.40	1.40
Silicone Emulsion LE-462 (50% A.I.) UCC	0.35	0.35
Arlacel C (Non-ionic surfactant) ICI Am.	0.15	1.25
Isopar C or E (C_7 or C_8 iso.paraffinics) Exxon Oil Company	2.00	33.00[c]
Lemon Oil, Technical Grade	0.75	0.60
Glutaraldehyde (50% A.I.) UCC	0.05	0.03
Sodium Nitrite	0.05	0.05
Deionized Water	86.00	44.67
Isobutane A-31	7.00	17.50

[a]Oil-in-water version.

[b]Water-in-oil version. (Better product; more costly.)

[c]Any n-paraffinic, iso.paraffinic, or multi-brancheate low-odor hydrocarbon may be used, at 12 to 36%. About 20% is an average.

flammable vapor in air is required for ignition. Air-tight compounding tanks and good ventilation is required.

A related product is the wood paneling cleaner, conditioner, and polish. Pre-finished plywood wall panels, natural wood kitchen cabinets, and similar surfaces have relatively thin varnished or lacquered surfaces compared with furniture, so that the use of water-based polishes like those just described would result in some water penetration of the wood, and the finish would be gradually lifted or peeled. As a result, these products are anhydrous and de-emphasize the use of wax-type ingredients. The formulation in Table 35 provides good gloss, sealing, and detergent resistance.

Car Windshield De-Icers

The windshield de-icer spray is a product representative of dozens of automotive aerosols. The most effective de-icer is methanol (CH_3OH), and it is used to some extent, despite its well-known toxicity and the corresponding need for special labeling under various U.S. government regulations, such as the CPSC regulations. Isopropanol [$(CH_3)_2CHOH$] and n.propanol (CH_3-CH_2-CH_2OH) are less hazardous but are less effective and more costly. Since a simple alcohol or alcohol/water de-icer would allow refreezing of the liquid to occur as soon as the alcohol was sufficiently diluted or evaporated, it is customary to add a certain amount of glycol to formulas. Here again, ethylene glycol (HO-CH_2-CH_2-OH) is the most effective, but it also is quite poisonous, so propylene glycol [HO-C(CH_3)H-CH_2-OH] is used instead.

If very thin ice films are dissolved by an anhydrous alcohol/glycol product, after which the alcohol largely evaporates, vision will be obscured by the heavy glycol layer that remains. To resolve this final problem, certain amounts of water are included in the formulas. The higher-quality products will have about 20%, while the economy types may have as much as 50 percent. Table 36 presents a typical formulation.

TABLE 35. WOOD PANEL POLISH FORMULATIONS

INGREDIENTS	FORMULA (%)
D.C. 536 Fluid (An aminofunctional polydimethylsiloxane copolymer - Dow Corning Corporation)	2.00
D.C. 200 Fluid (12,500 cstks) (Dimethylsiloxane polymer - Dow Corning Corporation)	2.00
Witcamide 511 - Witco Chemical Company	1.00
Isopar L and/or Isopar M - Exxon Company	26.50
Isopar K - Exxon Company	65.20
Fragrance	0.05
Isopropanol (anhydrous)	0.25
Carbon Dioxide	3.00
Pressure (460-mm Vacuum Crimp) bar at 21.1°C	7.40

TABLE 36. WINDSHIELD DE-ICER FORMULATIONS

INGREDIENTS	FORMULA (%)
Methanol - Technical Grade	54.00
Propylene Glycol - Technical Grade	18.00
Deionized Water	25.00
Morpholine	0.10
Span 80 or Igepal CO-410 Non-ionics	0.05
Sodium Benzoate	0.05
Carbon Dioxide	2.80

The Igepal CO-410 (Rohm & Haas Co.) surface active agent is present in the formula in Table 36 because it improves the wetting activity of the formula, allowing it to penetrate more effectively into fissures and cracks in the ice, and then between the ice and the glass, for faster removal.

PESTICIDE AEROSOL PRODUCTS

Pesticides consist of insecticides, insect repellents, disinfectants, rodenticides, nematocides, herbicides, and a host of other products designed to reduce or eliminate pests in size ranges extending from viruses to rats. All these products fall under the purview of the EPA FIFRA if they are made or marketed in the U.S. Other nations have similar regulations. When pesticide products are designed for use on the skin in the form of "outdoor lotions" that protect against solar radiation, poisonous plants, infections from scratches, and also contain insect repellant, the EPA still has control but may consult with other agencies, such as the FDA in this case, before giving pre-market clearance. Information has been presented earlier on the disinfectant cleaner and disinfectant/deodorant spray, which are regulated by the EPA in the U.S.

Insecticides

The insecticide was the first commercial aerosol product, used as early as 1944 for both military and domestic applications. These early sprays were true "aerosols" (unlike any of today's products, except one type) and used 85 to 90% of CFC-12 to disperse the pyrethrin-containing concentrates. The first major segmentation of this product form came in 1953, with the introduction of the bug killer: a coarse spray consisting of at least 75% kerosene-based concentrate, used for surface wetting, instead of the usual space spray format. By 1961, water-based space sprays came onto the market, and many years later this technology was applied to the surface spray as well. Also in the early 1960s, a "whole-house insecticide," or "total release indoor fogger" spray was developed, typically using 85% CFC propellants. Other specialty insect sprays were developed later in the 1960s. They included the wasp and hornet spray, pressurized with nitrogen or carbon dioxide, and which could throw a stream or streaming spray up to 6 meters. A number of pet-stock sprays were also introduced. Later, hormonal flea-control sprays, biocidal sprays, and other types were introduced.

The space sprays are now essentially all water-based, since the other formulations were too costly and could not compete with the obvious economies offered by combinations of approximately 65% water and 30% hydrocarbon propellant. The only exceptions are the total release indoor fogger (TRIF) and toxicant/propellant (T/P) sprays.

The water-based space sprays can be closely compared with the air freshener shown in Table 30, Formula A. By removing the perfume ingredient and replacing it with a toxicant blend, the transition is complete. The water-based space sprays include the flying insect spray, house and garden spray, patio fogger, and a portion of the TRIF products. As a unit, they make up approximately 55% of the insecticide aerosol volume.

The TRIF spray made a difficult transition during 1978, when CFC propellants were banned in the U.S. Since it is designed to be latched open and to discharge the entire contents of the can within two or three minutes, there is a greater inhalation and flammability hazard than is the case with most aerosols, which release only a few grams at a time. The flammability aspect related to two factors: the size of the container (and the number used at one time), and the degree of product flammability. When problems have occurred, they have been caused by gross consumer misuse; for example, when two or more large cans have been set off in a relatively small area containing an ignition source such as the pilot light of a stove (range and oven), gas-fired refrigerator or gas-fired hot water heater. Table 37 presents three forms of commercial formulations for these products.

The relative flammability of the TRIF sprays can be assessed by using a slight modification of the Department of Transportation (DOT) Closed Drum Test in the U.S. The 200-liter drum is laid on its side, with the open end closed off with a film of plastic. A candle is lit at the bottom and the spray is immediately introduced, using the test formula but a different valve more

TABLE 37. TOTAL RELEASE INSECT FOGGER FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)	FORMULA C (%)
Pyrethrum Extract - 20%	2.00	2.00	-
Piperonyl Butoxide; Technical	1.00	1.00	-
Emulsifiable Concentrate	-	-	8.00
Petroleum Distillates	12.00	12.00	7.00
Methylene Chloride	-	15.00	-
1,1,1-Trichloroethane	55.00	40.00	-
Deionized Water	-	-	50.00
Propane A-108	30.00	-	-
Isobutane A-31	-	15.00	35.00
HCFC-22	-	15.00	-

compatible with the test procedure than the "latch open" type. The number of grams of product sprayed into the drum until the Lower Explosive Limit (LEL) "poof" is reached and recorded. From that figure, the number of cubic meters that the dispenser can bring to the LEL composition is readily calculated.

Insect Repellents

The usual insect repellent is used to keep users from being bitten or stung by various flying insects. The most common ingredient is N,N-Diethyl-m-toluamide in concentrations of 15 to 30% of the total formula. Sometimes other repellents are added for protection against insects only partially repelled by the DEET active ingredient. They include MGK Repellent 11 and MGK Repellent 264 and are offered by the McLaughlin, Gormley & King Company, of Minneapolis, MN (U.S.). A typical formula is shown in Table 38.

Variations on Formula Type 26 include replacing the hydrocarbon propellant with 4.5% carbon dioxide, replacing the ethanol with isopropanol, and removing the three MGK products, while increasing the level of DEET repellent to about 30 percent.

The transfer efficiency from dispenser to skin or clothing is only about 55 to 65%, making other forms more attractive by comparison. Lotions and sticks are available, as well as roll-on forms.

PHARMACEUTICAL PRODUCTS

These products are generally perceived as those that are inhaled, injected, or otherwise inserted into the body to mitigate or control medical problems such as migraine headaches, asthma, hemorrhoids, etc., or to provide a contraceptive function, such as vaginal contraceptive foam. A few of these products have already been covered in the foams area of this chapter. The primary one that remains is the metered dose inhalant drug (MDID), which represents a U.S. market conservatively estimated at well over 100,000,000 units per year and served by at least 28 brand-named products. As is common with the rest of the aerosol industry, products are self-filled and also

TABLE 38. INSECT REPELLENT FORMULATIONS

INGREDIENTS	FORMULA (%)
N,N-Diethyl-m-toluamide (95% A.I. min.)	20.0
MGK Repellent 11	2.0
MGK Repellent 326	1.5
MGK 264	1.5
S.D. Alcohol 40-2 (Anhydrous)	54.9
Fragrance	0.1
Propellant A-46 16 wt % propane and 84 wt % isobutane	20.0

contract filled. One or more self-fillers also contract fill for their competitors. At this time, all of these products use one or more of the following propellants: CFC-11, CFC-12, and CFC-114. The volume of propellants used is approximately 1,900 kilotonnes (4,200,000 pounds) in the U.S. alone. Table 39 shows a typical published formulation. Others are suggested in U.S. Patent literature and other documents.

Use of hydrocarbon propellants for some of these products is not satisfactory because of production problems related to flammability, the oily, stinging taste they have when inhaled nasally or orally, and their very low density (considered from the standpoint of drug precipitation rates during use).

CFC-11 is slurried with the drug and one or more excipient materials, and this mixture is added to aluminum aerosol cans or bottles. They are then fitted with a ferrule-type meter-spray valve which is hermetically sealed to the container by a clinching or under-tucking operation. The CFC-12, sometimes mixed with CFC-114, is then introduced backwards through the valve.

CFC-11, with a boiling point of about 23°C, is unmatched by any other nonflammable solvent of acceptable toxicology. Its replacement will necessarily depend on the availability of one or more of the "future alternative" HCFC and HFC propellants due to come on the market in 1992 or 1993.

For the 90% of MDID products that use very finely divided microcrystalline drug particles (averaging from 3 to 5 microns), it is important to have a system of low solvency. Otherwise, the larger particles will get still larger and the smaller ones (because of their higher surface energy) will get smaller until they vanish. This disturbance will severely limit the product effectiveness. Even with the optimum particle size distribution, the body's defenses are such that only 7 to 12% of the drug reaches the target areas. With the formation of larger particles in the container, this could drop to below one percent.

TABLE 39. BETA-ADRENERGIC BRONCHODILATOR FORMULA

Ingredients	g/10.5 g Can	Percentage (w/w)
Terbutaline Sulfate (Drug)	0.075	0.714
Sorbitan Trioleate (Excipient)	0.105	1.000
CFC-11	2.580	24.571
CFC-114	2.580	24.571
CFC-12	5.160	49.144

The time frame needed for additional toxicological testing of the HFC and HCFC propellants, such as that being done in the Program for Alternative Fluorocarbon Toxicity Testing (PAFTT)I, PAFTT II, and PAFTT III consortium tests sponsored by the chemical producers, is one element of the new product development. Another is actual formula and package development and specifications writing. A third is the opening of each company's "New Drug Application" to the FDA, requesting an "Amended New Drug Application" (ANDA). The entire documentation is reviewed in such procedures, which typically take from 3 to 5 years to complete if there are no problems. One industry concern is that the FDA may not have sufficient staff to process approximately 27 concurrent ANDAs with anything like their usual timing. These considerations suggest that it would be to the advantage of chemical producers to cooperate in their efforts to have new products cleared by the FDA within the generally planned transition period ending about 2000.

The viability of new formulas depends on their solvency and toxicology. Preliminary results from PAFTT will be released in September 1989. Because of the uncertainty about HCFC-123, three possible formulas are suggested here for consideration (see Table 40).

The use of HCFC-124 is optional, since it merely serves to reduce the pressure slightly. The CFC-113 is used as an additive to the slightly flammable HCFC-141b to create a nonflammable blend for slurrying purposes. If the pharmaceutical firms and their fillers can handle a slightly flammable slurrying agent (pure HCFC-141b), there will be no need to use the CFC-113 (or CFC-11).

INDUSTRIAL AEROSOL PRODUCTS

There are numerous aerosols used only in industrial or institutional applications. Two will be considered here: a lubricant spray for pharmaceutical pill- and tablet-making rotary molding machines, and an industrial

TABLE 40. METERED-DOSE INHALANT DRUG FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B (%)	FORMULA C (%)
Drug (as a microcrystalline suspension)	0.5	0.5	0.5
Excipient(s)	1.0	1.0	1.0
HCFC-123	13.5	-	-
CFC-113 (or CFC-11)	-	4.5	-
HCFC-141b	-	9.0	13.5
HFC-134a	75.0 - 85.0	75.0 - 85.0	75.0 - 85.0
HCFC-124	10.0 - none	10.0 - none	10.0 - none

adhesive. For the first application, the products must be nonflammable, and leave only a Food Grade [Generally Recognized as Safe (GRAS)-Listed] residue on surfaces to be contacted by the pharmaceutical pill or tablet. A current formulation is shown below:

Rotary Tablet Machine Die Lubricant

Ingredients	Formula (%)
Lecithin (Soy Bean source)	2.0
Sorbitan Trioleate	0.5
Ethanol (Anhydrous)	2.5
CFC-113 (Especially purified)	70.0
CFC-12	25.0

An intermediate step could replace the CFC-12 with a mixture of 10 parts HCFC-142b and 20 parts HCFC-22, reducing the CFC-113 to 65 parts in the process. This would reduce the CFC content by 32 percent.

When the future alternative propellants become available, the formulations shown in Table 41 could be considered. Substantial testing of these prototype formulas in Table 41 would be required as a prerequisite to commercial use.

Adhesive Spray

A typical industrial product is the adhesive used to coat automotive gaskets before setting them in place on engine blocks or other equipment. Aerosol products have a substantial niche in this market area. A typical formulation is illustrated in Table 42.

TABLE 41. ROTARY TABLET MACHINE DIE LUBRICANT FORMULATIONS

INGREDIENTS	FORMULA A (%)	FORMULA B[a] (%)
Lecithin (Soy Bean source)	2.0	2.0
Sorbitan Trioleate	0.5	0.5
Ethanol (Anhydrous)	2.5	2.5
HCFC-123	77.0	-
HCFC-141b	-	55.0
HCFC-124	-	30.0
HCFC-22	18.0	10.0

[a]Formula B could replace Formula A if HCFC-123 does not become commercially available.

TABLE 42. GASKET ADHESIVE FORMULATION

INGREDIENTS	FORMULA (%)
Isopropanol	10
Resin 80-1211[a]	5
Stabilite Ester Number 3[b]	5
Methylene Chloride	50
Xylenes	10
Propellant Blend A-70	20

[a]Made by the National Starch and Chemical Company.

[b]Made by Hercules, Inc.

The product is sprayed onto the gasket while it lies on a waxed paper or other suitable substrate. After a minute or so, much of the methylene chloride will have evaporated, bringing out the stickiness of the resins. After another five minutes, the gasket is ready to be applied to the engine block or other item.

Part II - ALTERNATIVE AEROSOL DISPENSING SYSTEMS

SECTION 1

INTRODUCTION

An imposing number of packaging alternatives to the standard aerosol dispenser are available. Several use aerosol containers, but segregate the propellant gas, and employ a finger-pump, trigger-pump, hand-operated piston action, a metal spring, screw device, or other mechanism to dispense the product or form the propellant gas within the container as required. Others take the form of rather specialized, non-aerosol containers designed to enable the user to create air pressure or product pressure, or to operate screw-on finger-pump or trigger-pump metering valves. The pump-sprays, in all their diverse forms, represent the most widely used alternative. Such packaging options as stick applicators, pads, etc. offer alternatives to the aerosol system but do not provide sprays; these will only be briefly described.

A substantial number of aerosol alternatives will be described in Part II of this report, beginning with those that are most similar to conventional aerosols--and that may even be considered aerosols by various persons and authorities--and continuing with alternate packaging forms that bear no resemblance to aerosol products.

Definitions

The term "aerosol" was used by the scientific community at least as far back as 1838 to describe dispersions of liquids in a gaseous medium, such as fog, mists, and clouds, where the particles were true colloids, having diameters of approximately 0.005 to 0.200 microns (μ). Particles of this magnitude were able to remain air-borne indefinitely. The smallest particles are the same size as many larger molecules, such as starches, proteins, and rubbers, and this part of the definition has not changed over the years. But the high end of the size range originally defined as the limit of microscopic visibility, has changed greatly. The so-called "coarse aerosol" (to the physicist) now includes dispersions of particles ranging from 0.2 to about 20 microns (μ). Since the particle size distribution of commercial aerosol sprays is generally in the 1 to 100 micron (μ) range, at least some of the sprays meet the expanded classical definition.

Some early definitions of aerosol products were based on particle size. For example, around 1949, the U.S. Department of Agriculture (USDA) designated that the "true aerosol" insecticide was one in which at least 80% of the particles had a mean diameter of 30 microns (μ) or less, and in which no particle could have a mean diameter greater than 50 microns (μ). To meet these requirements, chemists had to design formulas with 80 to 85% or more of propellant. The rationale was that the spray particles had to be very small to remain airborne for two minutes to two hours to control flying insects. The products soon became known as space sprays.

At about the same time, the USDA introduced the "pressurized spray" concept for insecticides that were slightly more coarse. The mass median diameter of all particles had to be about 25μ, and some could be above 50μ. Because the larger particles fell to the floor in less than one minute, marketers had to use label directions that advised the user to spray an additional 25-50% more product into the air space of rooms.

Finally, about 1951, the "residual spray" insecticide was defined. Essentially all particles had to be larger than 50μ, so that such toxicants as Chlordane, Strobane and DDVP (dichlorphos) would not be inhaled to any significant extent. These were used only for spraying baseboards, doorway sills, wasp-nests, and other inanimate surfaces.

The piston-pump insecticide sprayer could dispense dispersions of particles about 25μ in size with deodorized kerosene formulations and those 20μ in size with the more flammable ethanol and isopropanol compositions. The finger-spray and (later) trigger-spray insecticides generally provided distributions of particles in the 30 to 80μ range. Consequently, much more had to be used for the control of flying insects, and the range of action was also much less than that of aerosol dispensers.

The confusion between "aerosol" (the colloid sol) and "aerosol" (the dispenser) has existed since the aerosol industry was born in 1943. In an internal report, the Academic Press Inc. publishing house mentioned that more copies of one of their new textbooks (Aerosol Science, C.N. Davies - Editor, 1966) had gone to recipients in the aerosol packaging industry than to the intended audience of physicists, physical chemists, and meteorologists, mainly because of the lack of contents identification in some advertising and promotional materials. The industry made an attempt to rename itself as the "Self-pressurized Dispenser Division" of the Chemical Specialties Manufacturers Association, Inc. (CSMA) but the proposal was defeated. Today, the words "aerosol" and "self-pressurized" product are used interchangeably.

For the purposes of interstate transportation, the U.S. Interstate Commerce Commission (ICC), now a branch of the Department of Transportation (DOT), defined the aerosol package in 1948 as follows:

"A sealed package containing base product ingredients, in which one or more propellants is dissolved or dispersed, and fitted with a dispensing valve."

Despite the fact that many self-pressurized products thought of as aerosols do not strictly meet this definition, nearly all are currently shipped under Section ORM-D of the tariff. (The definition has been modified slightly over the years.)

Other definitions are listed below without special comment:

CSMA Definition: "A pressurized sealed container with liquified or compressed gases so that the product is self-dispensing."

FDA Definition: "A package consisting of a container and valve, into which is added a base product and propellant, causing the dispenser to be under pressure, and able to discharge the product as a spray, foam, liquid, gel, or other form."

H.R. Shepherd (Book) Definition, 1960: "A container whose contents are expelled through an opened valve by means of the internal pressure of the materials contained therein."

P.A. Sanders (Book) Definition, 1979: (Also used by CSMA) "A self-contained sprayable product in which the expelling force is supplied by a liquified gas."

National Paints and Coatings Association (NPCA) Definition: "A self-contained package which contains the product and the propellant necessary for the expulsion of the former."

British Aerosol Manufacturers Association, Ltd. (BAMA), 1971: "As integral ready-to-use package incorporating a valve and product which is dispensed by prestored pressure in a controlled manner when the valve is operated."

Most of these definitions were created by one person, then approved by a committee or by a brief committee action. Some are ill-conceived or outdated and either do not cover all aerosols, or cover products not commonly denoted as aerosols. In a recent inquiry to the DOT, a product consisting of a mixture of Halon-1301/1211 (20:80) was finally judged to be a non-aerosol and denied the standard aerosol ORM-D exemptions because it contained no base product ingredients. Two materials other than propellant had to be present to be designated an aerosol. The prospective marketer finally added a drop of kerosene (a mixture of ingredients) to 13 Av.oz. (369 g) of the Halon blend, and is now selling the product.

At a recent industry meeting, representatives from the Metal Box Division (CMB) in England stated that they had persuaded British Aerosol Manufacturers Association (BAMA) and the FEA (Federation of European Aerosol Associations) in Western Europe that self-pressurized products placed in their "Bi-Can," a compartmented can containing an inner plastic bag for the base product, should not be considered aerosols. This would give them preferred treatment by the following transportation authorities:

- ADR European Agreement for the International Carriage of Dangerous Goods by Road.
- RID International Convention Concerning the Carriage of Goods by Rail (Berne 1961; Annex 1).
- IATA International Air Transport Association (Restricted Articles Board).
- IMCO International Maritime Consultative Organization (United Nations).

They asked for industry support in the U.S. No action was taken.

Another definition of an aerosol product that has often been published is as follows:

> "A hermetically sealed metal, glass or plastic container, fitted or able to be fitted with a valve, and containing a base product and/or a liquified and/or high-pressure propellant, able to dispense the contents in a controlled manner as either a spray, foam, stream, gel, paste, lotion, gas, powder or combination."

In the U.S., for the purpose of interstate transportation, aerosols are limited to 50 cubic inches (819.35 mL) in metal cans, or to 4 fluid ounces (118.28 mL) in non-metallic containers. The United Nations recommendation is 1000 mL for all products, and this is generally followed in Europe. In Japan and other countries, the capacity limit is 1400 mL, although other restrictions apply. A few countries permit "aerosols" up to 20 liters in capacity if made of steel. In the U.S., steel cylinders up to 40 liters in capacity are used for insecticide sprays, egg treating mineral oils, and other specialized applications. They are not considered aerosols. In some beauty shops, hairspray concentrates are dispensed from pressure tanks maintained at about 100 psig (7.04 bar) compressed air pressure at ambient temperature. The operator uses a thin hose and breakup nozzle for product applications. These products are also not considered to be aerosols.

SECTION 2

DESCRIPTION OF AEROSOL PACKAGING ALTERNATIVES

BAG-IN-CAN TYPES

The Sepro Can

In 1954, Croce patented a perfume spray in which the perfume concentrate and the propellant were contained in separate reservoirs (U.S. Patent 2,689,150). And in 1955, the Metal Box Company, Ltd. was granted a British patent for a device that would permit the dispensing of flowable products where the product and propellant were kept separate from one another (Brit. Patent 740,635). In 1958, the Continental Can Company, Inc. formally introduced their Sepro Can, which contained an accordion-shaped polyethylene plastic alloy bag inside a specially designed aerosol can measuring 1 1/8" by 6 1/8" (53 x 156 mm). The unit was filled by first adding as much concentrate as possible to the bag, then sealing the top with a one-inch aerosol valve. After that, propellant gas was injected through a small hole in the base section of the can and the hole was plugged with a short length of rubber cording. Only a few grams of propellant were needed to discharge from 175 to 250 grams of product (according to its density), since the two were kept separate by the bag. Also, the propellant would never be discharged during the lifetime of the can, but would remain inside until the empty unit was crushed, shredded, incinerated or rusted through in a dump site, except for an infinitesimal amount that might seep through the plugged and double seam can seals and escape into the atmosphere.

Cross-sectional views of the Sepro Can, a mechanized or pneumatic squeeze tube, are shown in Figure 2.

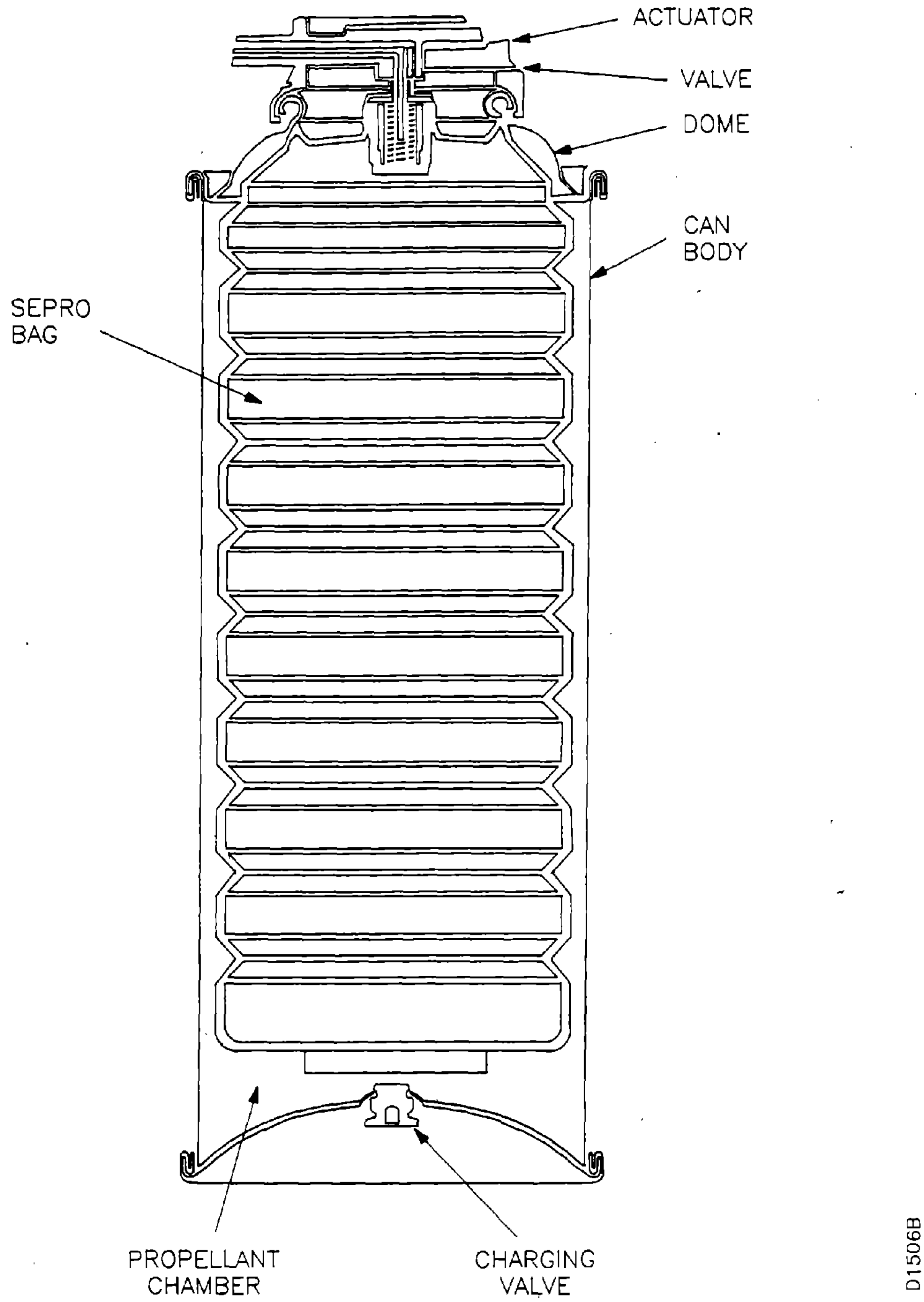


Figure 2. The Sepro Can

The Sepro Can, from the term "**Se**parate **Pro**duct and Propellant," was designed to permit gas-free dispensing and the dispensing of viscous products that had a positive yield point. It was hoped that this package would facilitate the growth of the aerosol business by allowing a new range of products to be packaged under pressure.

The standard aerosol cannot dispense products with viscosities much beyond 350,000 cps., since such chemicals and formulas usually have a positive yield point, or, in other words, exhibit shape retention. For example, if a toothpaste is filled into an ordinary aerosol can and placed under 100 psig (7.04 bar) of nitrogen pressure, an appropriate valve and spout will dispense the produce very nicely, although some slight expansion of the extruded paste may occur as dissolved nitrogen gas slowly forms almost invisible foam bubbles in the product. (This is too insignificant a feature to be observed by the casual user.)

Within the aerosol can, however, each actuation causes a further cavitation of the initially flat toothpaste surface. At a certain stage the cross-section looks as shown in Figure 3. The cavitation area will deepen with each additional actuation, until it reaches the bottom of the dip tube. At that point the nitrogen gas will exit in a fraction of a second, and the remaining product cannot be dispensed.

Toothpastes have been prepared without positive yield points, so that the cavity left after each actuation will slowly heal--or flatten out. However, they tend to drip off the toothbrush to some extent and will also leak out of the valve spout orifice onto the top of the container. Some of the nitrogen propelled (nitrosol) toothpastes of the early 1960s had spout plugs, connected to the spout by a fairly thin polyethylene filament. They were designed to be applied to the spout orifice after actuation, to prevent dripping. Sometimes the pressure created by releasing nitrogen gas caused them to pop out. One major marketer (Colgate) kept such a product on the market for about twelve years, selling 300,000 cans a year to persons who liked the dispensing system.

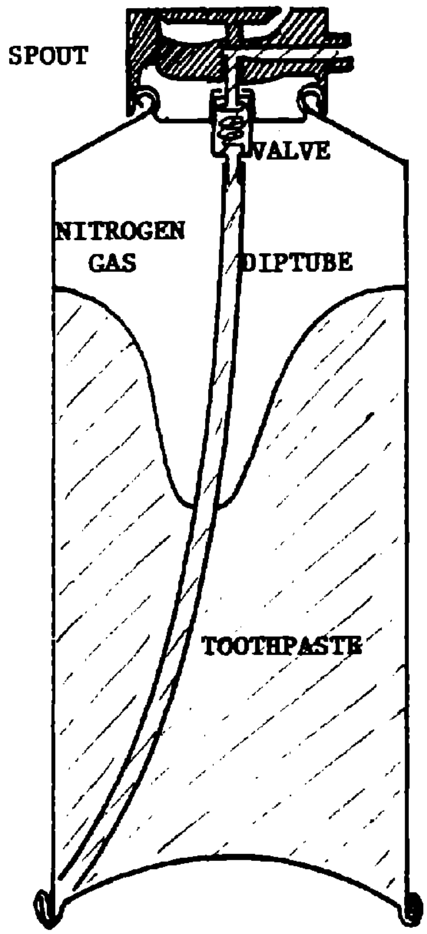


Figure 3. Ordinary Aerosol Dispenser with Toothpaste.
(About 15 percent Dispensed)

But a slowly diminishing business of this small magnitude was unappealing to Colgate and they finally dropped the item.

In the mid-1960s, the Continental Can Company developed and vigorously promoted to marketers the following four Sepro Can sizes:

202 X 214mm	(3-fluid ounce capacity)
202 X 406mm	(5-fluid ounce capacity)
202 X 509mm	(7-fluid ounce capacity)
211 X 604mm	(16-fluid ounce capacity)*

* Never produced commercially.

A major detraction was the need for marketers to spend about twice as much for Sepro Cans as for ordinary aerosol cans, as well as to install specialized "gasser-plugger" and other equipment on their packaging lines. The package also had a few quality problems. Except for "Edge," a patented gel-type shaving cream developed by S.C. Johnson & Son, Inc. in 1969, no major uses developed.

The evolution of the plugging technology went through several stages. At first, a gasser-plugger would inject a liquified or non-liquified gas into the filled can (1 to 7 g) and then ram the end of a 5/32" (4-mm) diameter lubricated neoprene cord or rod into the 1/8" (3.2-mm) diameter hole in the center of the can base. After insertion, the machine would cut the rubber cord off from the rest of the reel.

These early machines, required to perform three fairly complex operations in a sealed area, were production nightmares and generally the rate-limiting factor in manufacturing operations. Much later, engineering improvements were made to increase the viability of this sealing approach.

Then Continental Can Company announced an improvement known as the Nicholson Model 2 plug valve. It consisted of a solid rubber billet or plug, partly splined on the side wall, which was designed to fit part-way into the can hole during manufacture. In the filling operation, propellant gas was introduced through the splined channels, after which a small ram was used to force the plug fully into the hole, making an hermetic seal. This plug, with only slight residual modifications, is still in use today.

The early plastic bag designs were highly pleated or accordion-walled, and this caused problems when filling viscous concentrates such as pastes and gels. The Continental Can Company purchased a single-head and twin-head Elgin spin-filler, useful for filling these products, which they loaned to certain marketers and larger contract fillers to help in product development work. Larger machines, such as six- and twelve-head Elgins, were available. A very large Consolidated Equipment Company eighteen-head filler was modified for use by S.C. Johnson & Son, Inc. as a spin filler. Finally, the Pfaudler Mfg. Company later introduced a six- and twelve-head spin filler. The Consolidated and Pfaudler machines have a pressurized bowl option, for containing any vapors from shaving gels that contained isopentane $[(CH_3)_2CH\text{-}CH_2\text{-}CH_3]$ or other flammable or excessively volatile concentrates.

Every concentrate was found to have an optimum spin-filling rate, generally in the range of 400 to 1200 rpm. Below 400 rpm, the centrifugal force was often insufficient to effectively drive the concentrate into the pleated areas, causing unwanted air pockets to form and survive. Over 1200 rpm, concentrate vortexing would exceed gravity and product would be spun upward and out of the container.

During 1971, the products shown in Table 43 were being packaged in the Sepro Can dispenser.

The labeled formulas for the "Edge," "Rise," and "Foamy" gel shave creams are presented in Table 44. In accordance with Food & Drug Administration (FDA) regulations, these cosmetic products must list their ingredients in order of decreasing percentages; those present in concentrations of less than one percent may be placed in any order.

TABLE 43. PRODUCT MIX FOR SEPRO CAN DISPENSING

Brand Name	Marketer	Product Type	Sales (MM Cans/Yr)
Edge	S.C. Johnson & Son, Inc.	Gel Shaving Cream	11,500,000
Crazy Legs	S.C. Johnson & Son, Inc.	Gel Shaving Cream, for women	500,000
Shimmy Shins	Helene Curtis Industries	Depilatory	100,000
Shimmy Shins	Helene Curtis Industries	Moisturizing Cream	200,000
The Caulker	W.J. Jones & Company	Caulking Compound	Small
Tomato Catsup	Ellis & Associates Inc.	Tomato Puree Catsup	Small
The Meat Eater's Sauce	(Georgia Firm)	Barbecue Catsup	25,000
Steiner's Jewel Gel	Steiner & Company	Ablative Insulating Gel for Ring Repairs	20,000
Natural Honey	(California Firm)	Honey	35,000
Cook's Jolly Jelly	Cook Products Company	Three Jelly Products	30,000
Popcorn Oil	DeLorio & Associates, Inc.	Thickened Corn Oil; in three flavors	25,000
Corn Popper Oil	(Florida Firm)	Soy Bean Oil, several flavors	50,000

TABLE 44. CTFA LABEL INGREDIENT LISTINGS FOR THE THREE GEL-TYPE SHAVE CREAMS

Edge Ultra Gel	Rise Super Gel	Foamy Shaving Gel
Water	Water	Water
Palmitic Acid	Palmitic Acid	Stearic Acid
Triethanolamine	PEG-150	Oleth-20[a]
Pentane[b]	Diethanolamine	Triethanolamine
Sorbitol	Myristic Acid	Isopentane[b]
Fatty Acid Esters	Isopentane[b]	Lauramide DEA
Isobutane	SD Alcohol 40	Isobutane
Cellulose Polymer	Acetylated Lanolin Alcohol	Peanut Oil[a]
FD&C Yellow No. 10	Isobutane	Mineral Oil[a]
FD&C Blue No. 1	Fragrance	Hydroxyethylcellulose
Fragrance	PEG-90M	Fragrance
	FD&C Blue No.1	Coco-triglyceride[a]
		Menthol
		FD&C Blue No. 1
		D&C Yellow No. 10

[a]Lubricants, used to seal in moisture.

[b]The pentane and isopentane foamants are used in concentrations of about 1.4% of the formula.

The three formulas are quite similar. Each has the di- or triethanolamine ester of C_{14} to C_{18} fatty acids as the primary surfactant. Sodium and potassium fatty acid soaps are absent, although they are always seen in conventional shave creams. Cellulose, hydroxyethylcellulose, or high-molecular weight polyethylene glycols are used to achieve the gel structure. Most particularly, approximately 1.5% of low-pressure propellants are incorporated into the gel structure, so that the extruded gel can be "magically" converted to a heavy foam on contact with the warm surface of the palm or fingers or if touched and manipulated slightly. The original "propellant" was CFC-113 ($CCl_2F \cdot CClF_2$), but after the FDA ban in 1978 the formula was converted to use isopentane. Later, for a faster and more reliable transition, mixtures of n.pentane/isobutane (80:20) and isopentane/isobutane (90:10) became popular.

Around 1973, a regular shave cream called "Pour Homme" (For Men) was marketed in a Sepro Can. The shave cream contained 3.25% of Propellant A-46 (which is 15 wt % propane and 85 wt % isobutane), and the "exospace" (the volume outside the bag but inside the can) contained Propellant A-60 (32 wt % propane and 68 wt % isobutane). With a pressure ranging from 16 to 29 psi higher than the product at 70°F (1.1 to 2.0 bar at 21°C), the product was extruded at a reasonable flow rate, and since no propellant could ever escape from the concentrate into an expanding head space, as happens with all regular aerosols as they are used up, the foam density and overrun remained exactly constant for "Pour Homme" during its service life. After two years, the company was unable to obtain Sepro Cans to continue its operations and the product was terminated.

At present, the Continental Can Division of U.S. Can Company, Inc. is the only U.S. producer of this type of container. They have a capacity of 50 to 52MM units a year. The cans themselves are produced only on the firm's "Z-bar TFS Conoweld I" line at their fabrication/assembly can-making plant near Racine, WI. The line has a capacity of about 53 million units a year on a ten-shift-per-week basis, and sub-assembly units, such as the pierced base with loosely fitted plug, can be produced at only a slightly greater rate.

The plastic bottle or "bag," as it is generally called, is made at the company's Burlington, WI facility, using three "wheels" or individual production lines, each having a capacity of 17.5 million units a year on a three-shift, five-days-per-week basis. Originally, the bags were made of either polyethylene (LDPE) or of a particular "Conalloy" plastic alloy. The former type has now been eliminated. The current Conalloy bag consists of low-density polyethylene, nylon, and a proprietary binding agent produced by DuPont that makes the two plastics more compatible. The Conalloy bags mold better than LDPE types and have been used continuously since 1968.

While the discontinued LDPE had better resistance to moisture permeation than Conalloy, the latter is superior as a hydrocarbon propellant barrier. This characteristic became critical when Edge shave cream had to be reformulated in 1978 to eliminate the internal CFC-113 foamant and the external CFC-12/114 (60:40) blend ($CCl_2F_2/CClF_2 \cdot CClF_2$) in favor of isopentane and isobutane/propane (87:13), respectively. When hydrocarbon Edge formulas were packed in Sepro Cans with LDPE bags, traces of immediate foaming were seen in gels dispensed after as little as eight months of room temperature storage and five months of 100°F (38°C) storage. In contrast, when Conalloy bags were used, technicians could not detect instant aeration until after 14 to 16 months of storage and the permeability did not escalate to a consumer problem until the product had been stored 20 to 24 months at 70°F (21°C).

During late 1981, a 100% nylon bag became commercially available. It was a stronger, tougher bag than the Conalloy type. It was pre-form or parison molded at a substantially higher temperature than the Conalloy type, making it possible to fill Sepro Cans with very hot products, and even to sterilize them in an autoclave to the usual 252°F (122.2°C) if desired. After cooling to below 122°F (50°C), the Sepro Can may then be gassed and the bottom sealed. Advantages of the nylon bag are that much less plastic is needed, and the critical "T-tab" area at the bottom of the bag knits together very effectively and reliably, like the earlier LDPE bags but unlike the Conalloy type. Voids or thin spots have been a continuing problem of the Conalloy bags.

During 1983, the "Lamicon" bag was developed for Sepro Cans, using a Japanese process for the pre-form or parison blow-molding of multi-layered plastics. The wall of the Lamicon bag is composed of LDPE/adhesive/EVAc/adhesive/LDPE, wherein the EVAc stands for ethyl vinyl acetate polymer. EVAc provides an excellent barrier for oxygen and other gases. It has a good record in food bottles, and Sepro Can tests show the same good performance. It is also an excellent hydrocarbon gas and liquified gas barrier.

The Conalloy, nylon, and Lamicon bags can be effectively used with a great variety of products, but there are reasonable limitations, as with all packaging systems. Some are listed below:

- There may be problems with products whose viscosities are over 95,000 cps. (e.g., very thick molasses) at the discharge temperature:

  -- Nylon will take up to about 350,000 cps, but transport rate through even very large orifice valves may be slow.

  -- Clayton and Super-Whip valves have "huge" orifices available, if inverted applications are acceptable.

  -- Special Precision, Bestpak, and Beard valves are sometimes useful.

  -- Increasing the propellant pressure outside the bag is useful, up to the practical limit of 70 psig (4.9 bar) at 70°F (21°C). In contrast, regular aerosols can only handle products with viscosities up to 2,000 cps at room temperature.

- Products that exhibit pressure-induced syneresis:

  -- The application of hydraulic or pneumatic pressure to some liquid-in-solid products will cause the liquid to be partially squeezed out of the matrix. An example is peanut butter, where the peanut oil can be synerized out of the mixture, leaving a substantially stiffer bottom layer. Initial experiments have shown that regrinding the peanut fragments will reduce or resolve the problem.

-- When ordinary peanut butters are packaged in Sepro Cans (using nylon bags) the units operate well for the first few days, but then deliver increasing amounts of peanut oil, and after all this is discharged, the remaining paste is too stiff to extrude.

- Products that are highly lubricous:

-- A salad oil product can cause the rubber grommet and seal of the Clayton valve to force out of the valve cup and fly across a room. This does not occur with stem-type valves.

-- A silicone product managed to permeate the bag in micro-gram amounts over many months, ultimately lubricating a nitrile rubber plug to the degree that it popped out of the hole in the base section. Sepro Can storage at 122°F (50°C) exacerbated the problem.

- Products that are acidic:

-- Although vinegar (acetic acid based) products can be placed in Sepro Can bags and used in connection with valve cups that are laminated with polypropylene or lined with nylon, so that no direct metal contact is possible, the contained acetic acid ($CH_3 \cdot CO_2H$) can permeate through Conalloy and nylon bags and attack the tin-free steel (TFS) Conoweld I can surfaces. Reformulation with malic or citric acids is useful in some instances, since these do not permeate to a significant extent.

- Clear gel products that may have long shelf lives before use:

  -- Hydrocarbon propellants are able to permeate Conalloy and nylon bags sufficiently to render gel shave cream products substandard after 20 to 24 months at room temperature. The problem seems to be strongly reduced if Lamicon bags are used.

- Certain solvents are capable of bag degradation. A solution that included 64% turpentine slowly turned an LDPE bag into a semi-viscous mass, and one with a vegetable oil did the same at 122°F (50°C). Diethyl ether, an 8% sodium hydroxide oven cleaner base, boiled linseed oil, and cyclohexanol all act to slowly degrade nylons. The use of alternate bags is sometimes an answer.

- Products that must be hot filled:

  -- None of the available systems will fail when concentrates are filled up to about 145°F (63°C) and propellant is introduced at any time thereafter.

  \- If concentrates are filled between 145 and 160°F (63 and 71°C), the propellant must be limited to isobutane, nbutane or their mixtures, or over-pressurization will occur. Exception: Higher-pressure propellants may be used if the hot concentrates are given time to cool to 145°F (63°C) or less.

  -- Above 176°F (80°C) the Conalloy and Lamicon bags may distort or have a better chance of dissolving in certain concentrates. Nylon bags should be used in such cases, since they can withstand temperatures up to 280°F (138°C) with most concentrates.

Depending on bag size, bag composition, and, to a small extent, the product itself, Sepro Cans will dispense from 94 to 97% of the contents within the bag. The propellant outside the bag is not dispensed. In the U.S., only the dispensable amount of the product may be listed as the net weight. As a rule, the Sepro Can operates with far less propellant than any standard aerosol product.

Considering hair sprays, most conventional (single compartment) aerosols use from 22 to 35% hydrocarbon propellant, or about 35% dimethyl ether propellant in the formulation. For a corresponding Sepro Can of the 202 x 509 size, the amount of exospace propellant would be about 2% of the weight of the concentrate. Some coarsening of the product would result from this transition, since the usual "micro-explosive" effect of the propellant evaporation would be absent.

The Sepro Can may be operated in any position, since the bag is always liquid filled. In fact, during the concentrate filling step, care should be taken to fill the bag to the maximum, while allowing room for the valve mounting cup insertion into the throat without overflow. Small air pockets, when expelled, may sometimes make a "splat" noise and cause some products to spatter. Fairly costly inverted or "spray-anyway" valve options are not required for Sepro Cans.

As the product is used up, the bag collapses upward in a controlled way because of the circumferential pleat design. No bag pinch-off will take place. The latest pleat profile consists of gently rounded "V"-shaped indentations between 5/16" (8-mm)-high vertical wall sections. Compared with the earlier, more sharply indented "V"-shaped pleats, the new bags provide a more controlled collapse pattern, increased bag capacity and a generally increased ease of filling viscous concentrates. A minor objection is that the Sepro Cans become increasingly top-heavy during use, as the bag collapses upward. This is most noticeable with dense concentrates such as toothpastes.

A special one-inch dome section is required for Sepro Cans, with the opening enlarged from the usual 1.000 ± 0.004" to 1.021 ± 0.003" (25.40 ± 0.10 mm to 25.93 ± 0.07 mm). This recognizes the approximately 0.10" (0.25-mm) thickness of the Conalloy and Lamicon bags in that area, so that with bags in place the net opening will be correct for the standard one-inch valve cups.

In the case of the thinner nylon bags, an intermediate can opening is required.

The Sepro Can may be closed with any standard valve cup and standard crimping tools; e.g., collet and mandrel (plunger). Standard 1.070 ± 0.003" (27.18 ± 0.07-mm) crimping diameters may be used. However, the crimp depth must be made larger, to account for the bag thicknesses at the crown and at the point of hard contact. (Actually, both are crushed to thinner dimensions in the crimping process.) Favored crimp depths are in the 0.180 ± 0.004" (4.57 ± 0.10-mm) range.

The can uses a regular necked-in 201-diameter bottom, uniquely pierced with a 1/8" (3.18-mm) hole in the center and having an upward lip or flange projection into the can. The Nicholson Model 2, two-stage charging valve is supplied by the can-maker and inserted to the first stage (loose) position in the hole. The filler introduces the propellant through the valve's ports, filling the area between bag and can. Depressing the valve to its second position with a ram seals the propellant inside.

The fit between plug and can base is very efficient. The leakage rate is always less than 0.50 g per year, and often less than 0.05 g per year at room temperatures. Should severe over-pressurization take place because of heating, the plug will remain in place even if the can eventually ruptures.

Sepro Cans are equivalent to other aerosol cans in terms of pressure resistance. They can be hot-tanked at temperatures up to 170°F (77°C) if the propellant is isobutane. During hot tanking, the contents of the bag do not significantly warm up, since the gas-filled exospace and plastic barrier are effective insulators. However, because of the pressure exerted on the can by the propellant in the exospace, all DOT regulations are satisfied.

There is a wide choice of propellants in the U.S. The usual ones are isobutane or lower-pressure blends of propane/isobutane. Dimethyl ether might act to soften the bags. For two reasons, the high-pressure compressed gases, carbon dioxide (CO_2) nitrous oxide (N_2O), nitrogen (N_2), and ethane ($CH_3 \cdot CH_3$) are not appropriate:

There is no reserve against slow leakage. (In the case of liquified propellants, a small liquid pool is present to replace lost propellant gas by evaporation);

Pressures will diminish substantially as the bag slowly collapses during product use because the absolute pressure varies inversely with headspace or outage space volume. This can be shown by the following example:

-- The volume of the exospace is 40 mL. The initial pressure of carbon dioxide is 115 psig. After 80 mL of product has been expelled (about 1/3 of the total), what is the remaining pressure?

Initial Pressure is 115 + 15 = 130 psi-absolute

$P_{Final} = P_{Initial} \times V_{Final}/V_{Initial}) = 43.3$ psi-absolute

Final Gauge Pressure - 43.3 - 15.0 = 28.3 psig

The example shows that such propellants are unable to dispense the entire contents of Sepro Cans.

Practical propellants for Sepro Can gassing are the hydrocarbons: nbutane, isobutane, and propane, or their blends. Establishments unable to safely fill hydrocarbon propellants may wish to use such blends as HCFC-22/142b (40:60) for non-food items. As product viscosity increases, higher-pressure [up to 70 psig at 70°F (4.9 bar at 21°C)] blends of butanes/ propane may be preferred. The action of Clayton, Super-Whip, and other stalk-type toggle valves can be stiffer at these higher pressures because of resistance factors.

Sepro Cans are presently being made on only one production line in the U.S. It has a speed of 240 units per minute and averages 110,000 units per shift. It is scheduled to run at a maximum of three shifts one day, two the next, three the third, and so forth, allowing for maintenance during the third shift on every second work day. Considering 200 days of operation a year, the output is 52,000,000 units a year.

Changeovers, from the standard 202 x 509 size to the 202 x 314 sample size, for example, are very costly to the supplier, requiring about 5 days of downtime for both the can-making and bottle-making plants, and a similar period to change back. It would take an order of 5 to 100 million cans for this to be feasible, and the can-maker has so far sold all sample cans to marketers at about twice the usual discounted prices.

Quality problems that caused S.C. Johnson & Son, Inc. to reject as many as 30% of all "Edge" Sepro Can pallet loads during 1980 and 1981 were reduced to a 0.28% reject rate in 1984 and to a 0.21% reject rate in 1987. The quality problems included the following:

- Welding faults--lack of integrity due to the presence of cold weld areas on the can side seam.

- Crimp problems--lack of integrity due to offset parting lines on the bag neck lying against the curl of the can. Since the bag-to-curl interface has to seal pure hydrocarbon gas, with no solvent action to soften or swell the plastic--to help create a more effective barrier--offsetting is a very serious consideration. The offset distance is tightly controlled and measured frequently during bag production.

- Incompletely molded rubber grommet. Grommets are made on a complex, 98-cavity mold, and sometimes the rubber fails to fill the entire volume of each cavity.

- Weak tail tab on the base of the bags. Presently a thicker (and thus stronger) knit line is used, together with a recessed construction.

- Top seam problems. The top double seam cannot be tested during can production for hermetic integrity, because of the bag. For example, welded end cracking has caused problems in this area.

Despite the manufacturing complexities of the overall Sepro Can package, the Continental Can Division currently feels that it produces a very high-quality item, partly because of the insistence on quality by customers.

The 1989 pricing of Sepro Cans of standard size is as follows:

	100,000 Units	500,000 Units
Base Price	$360.34	$360.34
Coat/Print/Varnish (Outside)	9.89	9.19
Each Additional Print	3.14	2.61
White Dome	2.60	2.60
White Bottom	1.64	1.64

In 1989, there were reportedly twelve marketers or contract fillers in the U.S. who were capable of filling Sepro cans. All but two or three have relatively low-speed Terco, Inc. gasser-plugger equipment, generally rated at 40 cans per minute. One filler (Aerosol Services, Inc., City of Industry, CA) has two such lines.

Since 90 to 95% of the present product mix is the post-foaming, gel-type shave creams, where the concentrate contains 4 to 5 volume percent of very volatile hydrocarbon material [typically isopentane, boiling at 86°F (30°C)], concentrate preparation and filling can be dangerous. The major filler, S.C. Johnson & Son, Inc., chills the concentrate (without hydrocarbons) to around 38°F (4°C) in a closed system, after which the hydrocarbon blend is added. Because of the low temperature, foaming is avoided, even when agitation is applied. The finished concentrate is filled into cans under explosion-proof, well-ventilated conditions. Other methods meter the concentrate and hydrocarbon portions together under cold conditions just before the filling step. The option of adding the gas-free concentrate, and then the pure hydrocarbon blend--or of adding the gas-free concentrate, crimping on the valve, and then pressure loading the pure hydrocarbon blend--is seen as a possible alternative for less gel-structured formulations. These "looser" dispersions would allow intermingling of the hydrocarbon liquid within a reasonable number of days or weeks. Since the bags are completely full, hand or mechanical shaking of finished units is of relatively modest benefit. The process is best served by filling the concentrate (gas-free) in very warm 122°F (50°C) conditions, adding the foamant gas by Through-the-Valve (T-t-V), hot-tanking, and then mechanically shaking cans or cases of cans at the end of the line. The 1989 prices for several Terco, Inc. machines required for these functions are shown in Table 45.

The present sales outlook for Sepro Cans is uncertain. Post-foaming gel-type shave cream marketers are studying the option of a piston version of the same can size, and one has market-tested the concept. Because of the high price of the Sepro Can and the availability of improved versions of the piston can in both tinplate and aluminum containers, most of the limited activity in this field centers in the piston area.

Bi-Can

Around 1987, after extensive research, the Sutton Aerosols Unit, Metalbox Aerosols & Toiletries Packaging Division, MB Group, p.l.c. (England) launched their version of the Sepro Can. Except for a longitudinal bulge, their nylon bag fits snugly to the can body, leaving only a 1/8" (3.18-mm) high space at the top and a somewhat larger volume at the bottom for the exospace propellant. Several can sizes are available. One is 115/114-200 x 515 (50-mm inside diameter by 150-mm inside wall height), while another is 112/113-114 x 312 (45-mm i.d. x 95-mm i.w.h.).

TABLE 45. PRICES FOR TERCO, INC. GASSER-PLUGGERS (1989)

Production Rate[a]	Type Operation	Cost (Dollars)
40 c/min.	Rotary Indexing	$26,063
40 c/min.	In-line	$45,758
80 c/min.	In-line	$56,355
120 c/min.	In-line	$77,040
120 c/min.[b]	In-line	$88,600

[a]Bottom charging and plugging unit only, except as noted.

[b]Bottom charging and plugging unit, plus through-the-valve gassing of hydrocarbon foamant.

The standard closure is a 3.5-mm pierced hole in the base, which is sealed by a short length of 5.0-mm diameter 80-Durometer nitrile cord after propellant injection.

Before the formal introduction of the Bi-Can at the Interpack trade show in Dusseldorf, West Germany, Metalbox worked with Aerosols International, Ltd. (England's largest contract filler) for over two years getting them ready to produce Bi-Can products on a medium-speed line having a capacity of about ten million units a year. During 1988, the line actually produced about 3.5 million Bi-Can units. As in the U.S., nearly all the business was in the popular post-foaming shave cream gel area, with products by Gillette (well over two million units), Wilkinson Sword, Tesco, Marks & Spencer, and Medicare.

The Bi-Can (short for "Bag-In-Can") is now being promoted for additional applications, including "Nappi" coffee concentrate, two toothpastes, a line of artist's pigments, petrolatums, lithium greases, catsup and mustard, jellies, medicinal liquids, soft- to medium-viscosity caulking compounds, syrups, honey and flavored honeys, medicinal liquids, and cake icings. Baby oils and skin lotions have been demonstrated to customers.

Were it not for the high cost, and sometimes the relatively small size of the package, bag-in-cans might be a very high-volume item. The ability of these units to contain and deliver products is summarized below:

- Can deliver, as well as contain;
- Cannot be spilled;
- Can be made sterile by autoclaving, and will remain sterile during use;
- Can be packed essentially air free for ingredient stability;
- Can handle liquids with viscosities of 1 to 1,000,000 cps. at ambient temperature;

- Can be packed and maintained moisture free (important for moisture-polymerized functional organo-silicones, for example);

- Are not messy to use;

- Are highly directional in application (controlled spray);

- Can be used with container in any convenient position;

- About 98% of the contents can be dispensed--more than many other packs;

- No risk of product contamination by metals, except stainless steel valve spring (The Metalbox "Metpolam" laminated valve cup may be needed);

- Highly concentrated product forms can be dispensed;

- With proper propellant selection, such as nbutane, the package can safely withstand temperatures up to 212°F (100°C);

- Applicable to post-foaming gels, as are the related piston-can and Enviro-Spray bag-in-can packs;

- No concentrate evaporation is possible;

- The propellant is only 1 to 2% of the total contents for most products and is likely to be incinerated with the empty can;

- Can dispense product as a spray, foam, post-foam, liquid, paste, or gel;

- Available in 3- to 9-fluid ounce (30 to 226-mL) bag volumes;

- Bags with as many as four different materials in up to four layers (including aluminum) are available for maximum resistance to permeation, ensuring shelf lives of at least three years in tests to date;

- With the better bag shape and improved filling techniques, thick items can be filled without refrigeration or spin-filling options;

- Low-pressure mixtures of special properties may be packed, such as a water and dimethyl ether mixture, which provides high solvency and soon evaporates completely;

- The package is triply tested: during can-making, when the bag is inserted, and during the bunging or plugging operation;

- A wide range of delivery rates is available, depending on choice of product viscosity, exospace propellant pressure, and valve orifice sizes; and

- A total of 23 "Trimline" sizes are potentially available, from 100 to 1,114 mL.

Metalbox, now actually CMB Packaging, Ltd., formed by the merger of Groupe Carnaud, S.A. and Metalbox Packaging, Ltd. in 1989,, declares that the Bi-Can is not an aerosol. This view is upheld by the British Aerosol Manufacturers Association (BAMA), and several European regulatory bodies (such as COLIPA) that have published conclusions on this subject. Bi-Cans are presently being shipped within the United Kingdom as non-aerosol commodities.

Compack

Around 1973, Aerosol Services Moehm, S.A. of Switzerland (now ASM, S.A.) developed a Lechner™ aluminum aerosol can with a LDPE vertically pleated bag and a valve cup lined heavily with plastic. Several sizes were offered, with diameters of from 1 3/8" to 2 1/8" (35 to 52 mm). Product leakage at the complex interface of can bead, bag flange, and valve mounting cup was a problem. Products such as Blendex toothpaste and a paste-type shampoo concentrate lost marketshare and this forced the company to look for refinements.

Alucompack

This bi-compartmented aerosol used a very thin aluminum tube with a flat base and flanged top as the inner container. This eliminated the gas permeability that had plagued the previous design, the LDPE bag. Also, if the system was combined with a seal of epoxy resin at the crimp area, using air as the propellant, it offered a three-year shelf life, guaranteed by the supplier.

The inner tube, or "Alu-Bag," of D-1 (Heat-Killed, minimum temper) aluminum was generally 0.992 ± 0.003" (25.2 ± 0.08 mm) in diameter and typically 6" (151 mm) long, or about 1/2" (12.7 mm) shorter than the outer aluminum can. Under the 3/32" (2.4 mm) top flange there is a thin neoprene rubber gasket, which is the area that can be improved by sealing with epoxy. The valve cup is fitted with 0.040" (1.00 mm) neoprene or buna-N rubber gasket, called a cut (or lathe cut) cup gasket, since this affords a more reliable seal than the Weiderholder or other Flowed-In, water-based neoprene gasket types.

The aluminum inner tube offers more resistance to pneumatic crushing than its plastic counterparts; therefore, it is necessary to use a fairly high-pressure propellant in the exo-space between tube and can. At least 28 psig (2.0 bar) of pressure differential should be available or dispensing will be incomplete. The aluminum tube is (rarely) susceptible to a kinking type compressive distortion; therefore, it is useful to insert a length of polypropylene capillary tubing in it before filling with the concentrate. Typical dimensions are 90 to 95% of the length of the tube and 0.090" o.d. by 0.060" i.d. (2.29 x 1.52 mm).

The i.d. of the outer can is typically 30 to 35 mm, which means that the volume of the exospace is greater than that of the inner tube or bag. Air or nitrogen pressure can then be used, and the pressure will not decrease substantially during tube collapse, unlike the situation with Sepro-Cans and Bi-Cans. Since less than 1.0 g of air or nitrogen is used, the degree of hermetic sealing must be very good.

The Alucompack development was used for toothpastes, a caulking compound for bathroom crack and crevice filling, and three medicinal items. Aerosol Services, A.G. performed the filling. They developed a technique of adding hydrocarbon propellants, first strongly cooled, into the outer can.

Of the 3 to 4 grams poured into the can, perhaps 1.0 to 1.5 grams evaporated before the evaporation stopped. Meanwhile, the inner tube, smeared with epoxy, was slid through the one-inch (25.4-mm) opening and quickly filled nearly full with product. The capillary tube was inserted. The valve, without dip tube, was placed in position and hermetically sealed. When pouring isobutane, propane, and their mixtures into cans, these dispensers were never filled outside of Europe. Approximately 1.7 grams of liquid hydrocarbon are released when Under the Cup type gassers release aerosol cans, and this is the major charging method employed in the U.S. and Canada.

Micro-Compack

The third variant, by ASM of Switzerland, is a smaller version of the Alu-Compack, generally holding about 10 to 15 mL of product. Such products as a "small area" depilatory (for facial hair, moles with hair, etc.), an anti-wrinkle (Retin A) cream, and various medicinal ointments are filled in these small dispensers. The 13- to 20-mm diameter ferrule-type valve is attached by standard 18- to 24-tine mandrel clinching techniques.

Lechner (Types I Through IV)

The Lechner GmbH System I can was developed around 1974 and consisted of a vertically pleated LDPE bag in an aluminum can, sold with or without a nitrile rubber plug in a 3.5-mm hole in the base. The filler can pressurize and seal the can with a gasser-plugger machine, or, with the plug in place, with a syringe needle that penetrates the plug. The Aerofill, Ltd. firm in England is one supplier of syringe gassers; they claim their hardened steel needles can last for filling up to 60,000 cans. The needles are eventually weakened by dulling and abrasion from the filler substances in the nitrile rubber plugs.

System I is limited to LPDE, and (now) HDPE (D1018) bags in seven sizes ranging from 50 to 400 mL. Such products as antiseptic sprays, household and car cleaners, medicinal and veterinary products, contact lens cleaners, disinfectants, depilatories, and air fresheners have been sold in these packages. Despite the sales efforts of Lechner USA Ltd., nearly all these products are sold only in Europe.

The System II dispenser has been more successful. It uses an inner aluminum bag and outer aluminum can, with top double seam and a dome that may be either aluminum or tinplate. The extruded, cut off and flanged outer can and inner bag are fitted together and triple seamed to the dome. It uses base gassing as described for the System I unit. Introduced around 1978, it is available in 14 sizes (18 bar), two at 15 bar (217.5 psig minimum burst), and one at 12 bar (174 psig). The last size is the largest: 502 mL, which was originally conceived for holding highly acidic hair coloring paste and for use with very high-viscosity silicone-based caulking compounds for commercial uses, but it is now used to dispense a wide variety of products. One interesting use for both this and the Alu-Compack is as the power unit for a nail dispenser. A particular gas blend of allene and methylallene, having a pressure of 90 psig at 70°F (6.33 bar at 21°C), is filled to a capacity of 100% into aluminum bags surrounded with propane, which has a pressure of 108.5 psig at 70°F air free (7.64 bar at 21°C). A micro-metering valve located outside the can feeds a tiny amount of "MAPP Gas" to the firing chamber of a very small spring-loaded ram cylinder when a triggering mechanism is pressed. A minuscule spark plug explodes the mixture above the piston-ram, and the ram then moves outward to drive in a nail, separated from a nail-pack and held in position below the ram. In this way, nails can be driven into wood as fast as one can pull the trigger. A 3.99-fluid ounce (117.98-mL) charge of MAPP Gas can sink thousands of nails.

A number of topically applied medicines and drugs are under test in small versions of the System II dispenser. The 3M, Inc. firm uses it for their fuel injector engine cleaner, since it is important that only the liquid phase enter the engine for spark plug and upper cylinder area cleaning purposes. Prescription dental gels and gum cements are conveniently dispensed. One new drug under development in Europe requires autoclaving at 275.4°F (135°C). After the filled System II unit is processed, heated, and cooled, it is gassed and plugged.

The Lechner System III dispenser consists of a conventional aluminum can, but heavily lined in such a way that the lining adheres tightly only at the crimp and upper dome area. The rest is very loosely attached. When the can is filled with concentrate and sealed, gas is injected through the hole in the bottom, causing the bulk of the lining to separate from the can surface and become, in effect, a bag. The base hole is then plugged. (Syringe filling cannot be done for fear of perforating the adjacent bag material.)

The modified polyolefin lining is suitable for a wide range of products. In fact, virtually any cream, gel, lotion, ointment, paste, or liquid now packed in a plastic tube or bottle can be more conveniently packed in the System III. At least 98% will be discharged.

Finally, the Lechner System IV is a modification of the System II, that improves on the relatively poor aesthetics of the triple-seamed dome design. It looks like a standard aluminum (one-piece) aerosol can. The larger version with a 1" (25.4-mm) opening will be available by October 1989, and smaller ones, using a 20-mm ferrule type valve, will come onto the market about March

1990. They will have a 0.98" (25-mm) diameter at first, but other diameters will be available later on.

The most significant of the Lechner developments is the System III dispenser, since it eliminates the preformed bag as such, and thus eliminates about a third of the component cost. This considerable economy should do much to stimulate volume growth of the two-compartment dispensing system.

Presspack

In 1976, this vertically pleated medium density polyethylene (MDPE) bag in aluminum or tinplate can development was completed by a West German firm in Hamburg. By the following year, two West German and one French firm announced they were ready to supply it commercially. However, because of seepage problems around the crimped seal (especially in the case of the aluminum cans), the dispensers were sold in relatively small quantities for about two years and then discontinued.

Other Bag-In-Cans

A number of additional bag-in-can designs have not achieved commercial success, sometimes in spite of excellent designs. One of these, developed in California and taken over by the (then) American Can Company, used a "cup" of polyethylene or laminate structure, attached via the top seam of a regular tinplate can. Production problems consisted of trying to uniformly air blow the plastic cups into waiting "domeless" cans, and trying to eliminate the "Z"s or "switchbacks" that occurred over the flange. When these triple thickness areas of plastic were wrapped into the top triple seam, actually a sextuple seam resulted, which leaked slowly or latently at the fold interfaces. The companies eventually halted product development.

PISTON CANS

As with the Sepro can, this compartmented package requires less propellant than a conventional aerosol package. Probably the first commercial piston can was developed in 1961; it contained about 4 Av.oz. (113.4 g) of Brylcream in an aluminum two-piece container with a free piston of medium-density polyethylene (MDPE).

Until about 1988, there was only one piston supplier in the U.S., the American Can Company (now the American National Can Division of Pechiney, S.A.), who supplied a two-piece aluminum Mira-Flo container. There are several in Europe and at least one in Japan.

During 1974, a drawn-and-ironed two-piece steel can was manufactured for the U.S. Borax and Chemicals Company's "Boraxo" waterless hand cream. The can was a seamless steel type, with top double seam. The problem with soldered and other welded side seam steel cans was that the polyethylene pistons could not fit the can wall snugly in this side-seamed area, and this caused "blow-by" of the gas past the piston wall and into the product, where it usually dissolved and lost its pressure. In fact, aluminum cans with wall dents were probable candidates for blow-by problems. During 1986, innovations in side-seal technology created the smooth side-seam profile, improving on earlier constructions of the "stepped" type.

The tinplate or tin-free steel (TFS) cans are probable candidates for piston can modification. They are approximately 20% less costly than aluminum and are available in sizes of 100-mL to 1114-mL total capacity. The metal is also harder and less vulnerable to pre-filling or post-filling denting problems.

The Mira-Flo Can

Experimental piston cans date back to 1956, when Crown Cork & Seal Company used a crude piston, over a large, compressed, steel spring to dispense various food products from their 202 x 406 Spra-tainer can. The spring provided backup pressure in case of propellant leakage. American Can Company began work on a two-piece 202-diameter aluminum can about 1960, and in 1962 they introduced their Mira-Spray (single compartment) and Mira-Flo (piston-type) 202 X 406 containers. The Mira-Flo had a 9/64" (3.57 mm) punched hole in the base, suitable for gas injection followed by plugging with a cord of 70-Durometer neoprene rubber.

The new cans were made at a plant that had an initial capacity of 38,000,000 units a year. Since the price of the Mira-Spray can was somewhat higher than that of the highly similar, steel, two-piece Spra-tainer made by Crown, sales were very poor.

American Can Company promoted the Mira-Flo cans, which were made on the same production line as the Mira-Spray cans, except that an LDPE piston and pierced base section were inserted. Samples containing domestic and imported cheeses were shown to Kraft, Nabisco, General Foods, and others from 1961 through 1963. Samples containing oleomargarine and thick chocolate syrup were shown to Mazola and Bosco product managers at the Best Foods Division of CPC International Inc. An experimental margarine sample, prepared at the American Can Company's Barrington, IL Research Center for the Land O Lakes Co., Inc. survives today, works well, and still contains product that has a good, fresh taste after 27 years.

After a few years, the capacity of the production line was reached: approximately 1,000,000 Mira-Spray cans for various small uses (such as air fresheners), 33,000,000 Mira-Flo cans with various types of cheese, and 4,000,000 Mira-Flo cans with various colors of Pillsbury's Cake Topping for creating decorative designs and/or messages on cake icings. The toggle-action Clayton Corporation food valves were supplied with several alternative actuator tips (in the case of the cake toppings) to create extrusions with star shapes, ovals, etc., in addition to the standard round ribbon. Instead of the more costly aluminum option, American has turned to the welded tinplate piston can.

While many fairly complex piston profiles have been developed (mainly in Europe) over a thirty-year period, in 1987 American pioneered the "free-floating type: a piston that had to expand slightly to reach the can walls. It requires the product to have a viscosity of over 12,000 cps at ambient temperatures. The novel pistons use a "gasket" formed by the product itself to effect the seal and inhibit gas by-pass.

The second innovation was commercialized in late 1986. Known as the "umbrella valve," it is a form of rubber plug shaped like a mushroom. It is applied from inside the can bottom. Small ears prevent the plug from being pushed into the can. The larger umbrella top is flexible enough to compress upon insertion. Once the plug is in the can, the internal pressure forces it downward, making a tight seal. The new valve allows filling speeds of up to 360 cans per minute.

Disadvantages of piston cans are that they require products of reasonably high viscosity that do not distort the piston. Piston by-pass (or blow-by) and permeation can cause problems by reducing the quantity of gas below the piston and perhaps by causing foam generation in the product. If the product is not compatible with the can, this can be a bigger problem with piston cans than with bag-in-can types because of the direct exposure of can surfaces to the product. New, very heavy linings are being developed by CMB Products, Ltd. and others to counteract this shortcoming. Some of the linings are bonded polypropylene approximately 0.010" (0.25 mm) thick, and they can also be used for the double seam sealing material.

Other Piston Cans

Piston cans using aerosol containers have been marketed by Advanced Monobloc, Ltd. (Division of CCL Industries, Ltd., Toronto, Canada), the Continental Can Group of United State Company, Inc., Boxal/Alusuisse, Cebal/Pechinery, S.A., Hoell, GmbH (Hamburg, West German), Rocep Pressure Packs, Ltd. (Glasgow, Scotland) and a firm in Japan. Except for the Rocep units, most are typical piston cans and conform to the description of "Mira-

Flo" units. Perhaps the largest manufacturer is the U.S. Can Co., since they now have a considerable share of the shave cream business.

Rocep cans are unique in that they are often quite small, such as 1" (25 mm) in diameter, and sealed with a 22-mm type ferrule valve. However, the main difference from others is that they use a double piston: two rather shallow types, one below the other, with the small space in between filled with mineral oil. The purpose of the oil is to capture and retain any propellant that penetrates through or around the lower piston, so that it will not go further upward and get into the product. Another unique feature is the "lever pack" package design, where the valve turret head is turned varying degrees on an eccentric track to control dispensing rates. Dispensing can then be actuated at various rates by depressing a 3 to 4" (76 to 101 mm) wire profiled lever against the can. This type of control is perfect for sealants, among other products.

Silicone acetate or silicone aminofunctional caulking compounds, which turn to a rubbery mass when brought into contact with humidity or moisture illustrate this product type. These products cannot be allowed to contact the liquified propellant or various degrees of foaming would take place as they were dispensed, leading to a strange-looking and less-effective seal. Under such trade names as "One Tough" Silicone Sealant blister packs containing three-ounce (80-g) piston cans are being sold at $5.95 to $6.95 each. Standard trigger-type caulking gun packs with twelve times as much of the same product are sold for $4.00 to $4.50 in the same stores.

An interesting alternative to the piston can is a pressurized pack designed to clamp onto one end of a standard caulking canister, filled with organo-silicone, acrylic, butyl or thiokol sealing compounds. An independent plastic piston is pressed into the cylinder by finger-pressure on an actuator. When the finger pressure is released, the gas pressure is automatically discharged upward, out of the orifice in the actuator. This instantly stops the flow.

The Rocep package uses a nonflammable mixture of HCFC-22/142b (40:60) for a pressure of about 83 psig at 70°F (5.85 bar at 21°C), including the partial pressure of trapped air.

A major problem developed when the relatively high pressure and solvent action of the propellant blend softened and squeezed the neoprene plugs out of the pierced holes in the tinplate can bottom, thus depressurizing the units. Short of using CFC propellants, there is no lower-pressure, nonflammable propellant currently available. The issue was finally resolved by moving to a slightly thicker nitrile plug and punching the hole in such a fashion that a slightly ragged lip was formed at the inner rim of the hole to act as a barb. Even so, extended storage at 130°F (54.4°C) will cause expulsion of the plug. Recent findings suggest that a trace film of mineral oil (from between the pistons) is a contributing factor.

The final difficulty with this package is that the container itself is composed of a special aluminum top and wall extrusion, but the base is of tinplate. An uneasy junction of these two metals at the bottom double seam is produced after the silicone product and double piston assembly are added. The tinplate tends to cut into the much softer and thicker aluminum, resulting in a 6.2% leakage rejection rate at the factory hot-tank tester. Technology exists to double-seam dissimilar substances, even plastic container walls to tinplate end sections, but it is not very effective for small-diameter closures such as the 1" (25.4-mm) diameter container.

Apart from the silicone-based specialty bathroom tub and tile sealants just discussed, no other products have yet been commercially produced in this packaging form. The high production cost, partly due to high scrap rates, is considered to be a major factor.

The Boxal Pump Dispenser

During the International Packaging Exhibition (Pakex 89; Birmingham, England; April 21, 1989) the Boxal Group, a member of Alusuisse Packaging

Division, showed their standard piston-type aerosol can, as well as a new, propellantless version that operates on a vacuum suction principle.

Using a custom-made valve by Coster, S.A. and a standard aerosol-type aluminum can with inner piston and perforated bottom (but no plug), the unit provides a metered flow of product whenever the actuating spout is operated. Lotions, creams, and pastes may also be dispensed.

When the pump actuator is depressed, a low vacuum is created in the product compartment. Through the hole (1/16" or 1.6 mm) in the base, atmospheric pressure then presses the HDPE piston upwards a small distance. The pump is constructed to prevent any contact between product and air until the material is discharged from the dispenser.

The pump stroke volume can be adjusted according to product characteristics and according to marketer requirements. Partial strokes will extrude correspondingly less product than full strokes. Because the pressure differential (between a partial vacuum and normal air pressure) is relatively low, the unit is not suitable for highly viscous products. They would emerge too slowly for customer satisfaction.

The development is not inexpensive, due mainly to the cost of the specially designed Coster, S.A. pump-action valve. It does provide a new and attractive packaging form for creams, gels, pastes, lotions, and other low-to-medium viscosity products in the cosmetics, toiletries, pharmaceutical, and food areas, usually giving those products prolonged shelf lives in comparison with packaging in jars or bottles. Evaporation, air oxidation, fragrance deterioration, spillage, and breakage are all avoided. The products can be filled on standard aerosol equipment at high speeds. From 96 to 97.5% of the material can be dispensed. In the U.S., unlike aerosols, the actual content (in fluid ounces), rather than the dispensed weight, is the basis for the declaration of contents on the label. However, labeling requirements will vary with the country having jurisdiction.

In one instance, an aqua-colored, rather viscous specialty shampoo was found to change color rapidly, toward green, then olive green, and finally yellow when packed in glass and exposed to sunlight. No color change has yet been seen in this product when packed for eight months in the Boxal pump dispenser.

INDEPENDENT BAG-IN-CAN SYSTEMS

During the late 1950s, inventor Ellis Reyner began to introduce aerosol marketers and fillers to his patented process for a product designed to permanently separate the propellant and product. In its simplest form, his innovation consisted of a plastic pouch, to be inserted in an aerosol can, either before or after filling with the concentrate. The pouch contained two chemicals: sodium bicarbonate ($NaHCO_3$) powder and a 50% solution of citric acid [$C_3H_4O(CO_2H)_3$] in separate burstable tubes. When the two chemicals come together, during a deliberate rupturing process directly ahead of the valve insertion and sealing operation, they chemically react to produce various sodium citrate salts and carbon dioxide (CO_2) gas. The outer envelope of the pouch remains intact, but it swells as a result of carbon dioxide pressure and presses against the can and the contents, so that when the valve is actuated, product flows out of the can as a coarse (non-aerated) spray, as a gel, paste, post-foaming gel, stream, or foam.

A problem with the early developments was that the bag was subject to gas permeation, stress cracking, product influences, and imperfect welding. These problems were solved by using laminates, often including a core layer of 0.0005" (0.013 mm) aluminum foil to almost totally eliminate any permeation. A less-effective barrier material is Mylar (polyethylene terephthalate - biaxial), which also adds considerable strength to the bag.

A second problem was that the bag could initially swell up only to the volume of the gas space over the concentrate. Because of various government regulations limiting aerosol pressures to about 180 psig at 130°F (12.68 bars at 54.5°C), the practical maximum pressure that the bag could exert at room temperatures was 142 psig (10.0 bars), and many marketers were more comfortable with 60 to 80% of this level. Following is an example of the pressure decrease during use that would take place for a typical product:

Product:	Toothpaste.
Volume Fill:	250 mL of toothpaste, 10 mL for pouch, and 140 mL for head space over the toothpaste.
Pressure:	140 psig at ambient temperature - initial. (9.86 bars)
Note:	Head space air compression to about 10% of original volume, plus absorption of some of that into the toothpaste, is not considered here. (Can be reduced by vacuum crimping.)

After the essentially complete discharge of toothpaste, the pouch volume will increase from 10 mL to 400 mL.

After the initial step of gas formation in the bag, it swells to 140 mL and has a pressure of 155 psi-absolute at ambient temperature.

Using Boyle's Law, the pressure drop during toothpaste expulsion will be:

$$P_f = P_i \ (V_i/V_f) = 155 \ (140/400) = 54.25 \text{ psi-absolute}$$
$$P_f = 39.25 \text{ psig } (2.76 \text{ bars})$$

Thus, the gauge pressure at ambient temperature is reduced from 140 to 39 psig (9.86 to 2.76 bars).

Repeating this study using an initial gauge pressure of 100 psig, would result in a final (can empty) pressure of only 25.25 psig (1.78 bars). This degree of pressure drop will result in significant decreases in delivery rate, especially for viscous products of positive yield point, during package life. This drop can be reduced by using what has been termed a "functional slack fill" of product, such as a 50-volume percent quantity, but this increases the cost per unit weight or volume of product and has other disadvantages.

Around 1975, the Grow Group, Inc. became interested in the Reyner system, thinking it could be refined to deliver a certain amount of gas at the onset, and that maintenance amounts could be provided as needed during use. After a research period lasting two years, the Grow Group announced the acquisition of Reyner's interests and the formation of Enviro-Spray Systems, Inc. to promote and sell the improved pouches and filling technology that had been developed.

The pouch now contained one fairly large inner container of 50% citric acid solution in water, plus six other much smaller containers. The larger receptacle could be torn or ruptured, either by striking the inserted bag with a small ram, or by the action of the vacuum crimping operation, releasing the contents and generating from 60 to 100 psig (4.2 to 7.0 bars) of carbon dioxide gas. As the product was used, the bag expanded as the head space expanded, and at a pre-engineered point the first smaller compartment of citric acid solution was breached. This returned the pressure to the original level. The process was repeated until the last citric acid receptacle had been ruptured.

With this sort of arrangement, the pressure could go (for example) from 100 psig to 80 psig, back to 100 psig, down to 77 psig, up to 103 psig, etc. as many times as there were citric acid receptacles. The relative complexity of having pressures of over 60 to 80 psig (4.2 to 5.6 bars) was questioned during the development of this system, as was the need for six maintenance system bags. Four of these appeared to be adequate, and future editions of the pouch ultimately used only four.

Other refinements include adding a flow tube, which consisted of a suitable length of aerosol valve dip-tubing so that the expanding pouch would not press hard against the middle or upper potions of the can wall and cut off or trap product below that point, keeping it from being discharged. Finally, the reservoir of sodium bicarbonate was contained in a water-soluble polyvinyl alcohol plastic, so that when the water-impermeable membrane between the primary citric acid sack and sodium bicarbonate compartment was deliberately ruptured by ram or vacuum action, the pouch would not instantly inflate, but would be delayed for one minute to allow time for the valve crimping (or sealing) operation.

Since the bag would be expected to inflate after the package was sealed, a way had to be found to authenticate that it had actually expanded. On production lines this was done by means of X-ray based level measuring equipment. Pressure measuring could be performed on a laboratory or statistical production quality assurance scale, and this also showed if only the main citric acid receptacle had ruptured. One problem with the system, even in units produced in 1989, is that two or more of the citric acid containers can rupture if there is a problem with bag quality, resulting in excessive internal pressures.

Figure 4 depicts a slow-speed aerosol line, using semi-automatic pouch-stuffers, rated at about 18 units per minute for each of the two machines in use. The rest of the line is fairly standard, except for the level checker, which is used to ensure pouch inflation.

The preferred valve is the Precision Valve Corporation Model 1-NN, with a 2 X 0.5-mm stem slotted "Enviro-Spray" type housing. Any type of actuator button or spout may be used. The standard pouch is designed to be used with a 202 X 514 (53-mm diameter X 300-mL) can with a 170-mL product fill.

The firm suggests the following product possibilities:

- Air Fresheners;
- Plant Sprays:
  - Leaf Shines,
  - Aphid control,
  - Fertilizer Concentrates;
- Petroleum Jelly (for example, for babies);
- Bathroom Cleaners;
- Toothpaste;
- Post-foaming Gels (as shave creams);
- Metered Dispensing (micro and macro);
- Toppings;

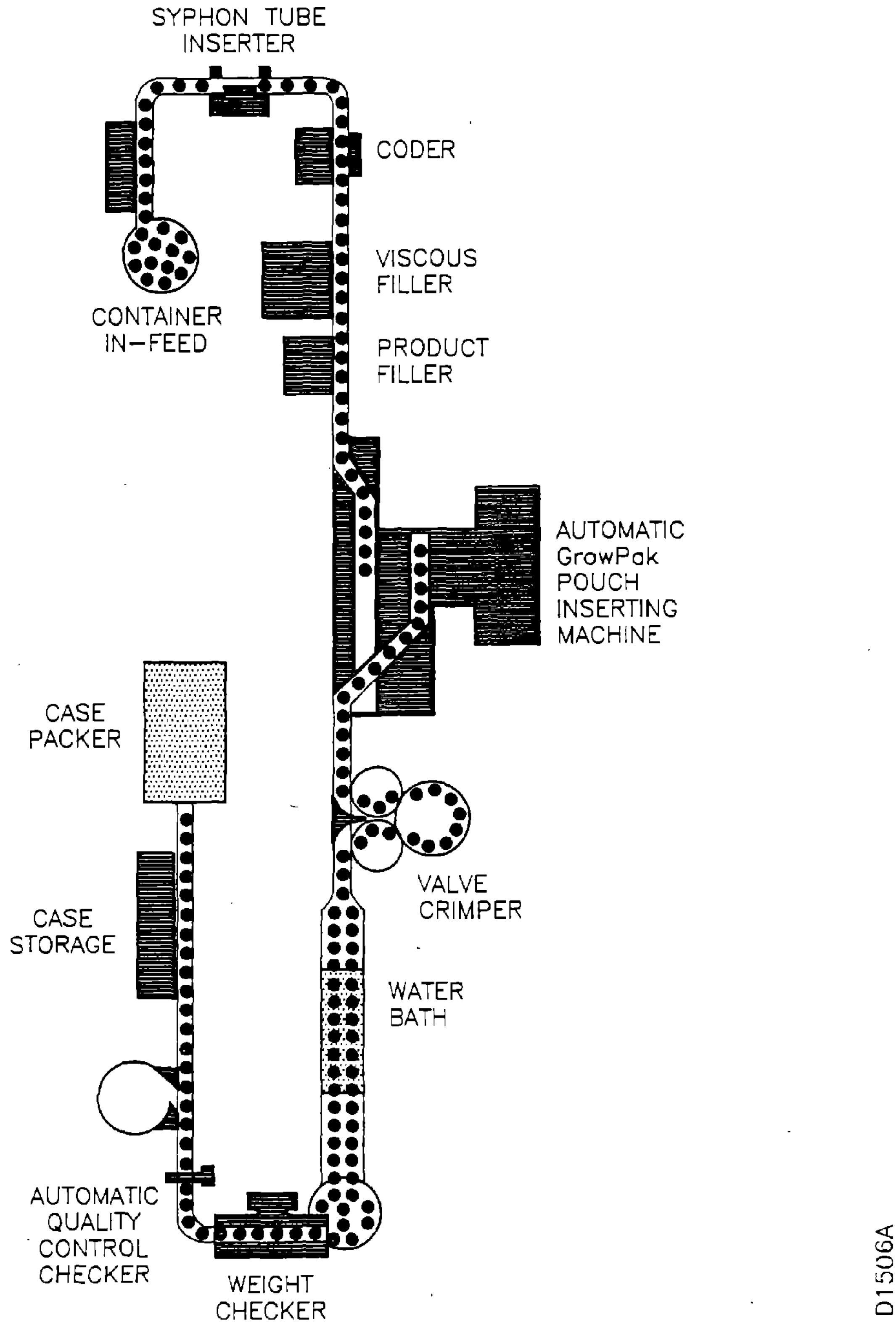


Figure 4. Slow-Speed Grow Pak Packaging

- Cheeses or Snack Items;
- Waterless Hand Cleaners and Related Lotions;
- Pet Care Items;
    - -- Groomers,
    - -- Shampoos - optionally insecticidal,
    - -- Flea & Tick Sprays (soundless);
- Cake Decorations;
- Industrial Maintenance Items, including lubricants;
- Selected Coatings;
- Furniture Polish (in lotion forms); and
- Mustard, Catsup, Purees and so forth.

Those products actually marketed in the Enviro-Spray System include the following:

- Tomato and Vegetable Insecticide;
- House Plant Insecticide;
- Rose & Flower Insecticide;
- Flea & Tick Spray for Dogs;
- Flea & Tick Repellant Spray for Dogs;
- Spray for Cats - Insecticide;
- Leaf Shine for Ornamentals;
- "Le Gel" by Williams (Beecham) Shave Cream;
- "Kouros" by Yves Saint Laurent;
- "Algipan" by Labaz Sanofi- Rubifacient Cream;
- "CCRF" Tomato Paste, Tomato Ketchup, and Mustard;
- "Mist & Feed" Foilant Nutrient Spray; and
- Beecham Caovel Pet Insecticide Spray.

In 1986, costs were $3.59 to $8.99 for cans ranging from 7-Av.oz. (200-g) to 32-Av.oz. (946-g) net weight. Containers were also sold for such specialties as institutional "gallon-size" insecticides, the pressurization of low-gas beer kegs, soft drink dispensers designed to operate under "no gravity" conditions in the NASA space program, etc. The pet sprays benefitted from the soundless delivery of the Enviro-Spray dispensers, since pets can hear and are distressed by the very high-pitched sound of standard aerosol sprays, except for those pressurized by air or nitrogen gases.

The second largest Enviro-Spray in Europe is a line of four food products by C.C.R.F. (France), under the brandname of Claude Vetillard. They include Tomato Puree, Double Concentrated 28% Mustard "Forte de Dijon," and Tomato Ketchup, packed to 280 g (250 mL) in metal box "Slimline" cans measuring 57 X 164 mm. Each is fitted with a Precision valve and "captured plug" spout. After 27 months, some cans of the Tomato Ketchup have shown a slight seepage of the product at the juncture or top and side seams. With appropriate adhesive-backed formula and precautionary stickers, these cans have made a modest entry into the more expensive U.S. specialty shops, such as those at airports and major hotels.

PUMP SPRAYS - ASPIRATOR TYPES

Pump-sprays have taken many forms. There are those whose pressure is generated within the meter-spray valve, and others (much rarer) whose pressure is produced in the container by various means. In the unique "Pre-Val" unit, developed by the Precision Valve Corporation (1975), a glass or plastic jar is filled with product and then sprayed out by aspirating it up a dip tube leading into an upper "Pressure Pack" containing a liquid propellant. When the valve button is depressed, propellant gas is discharged, sucking up a certain amount of the concentrate and discharging it as well. The usual ratio is about 4 to 1, so that approximately 400 g of concentrate is dispensed by 100 g of a hydrocarbon blend. No solubility of propellant and concentrate is necessary. If the concentrate might dry in the valve orifice to form a solid clog, or after use, the jar portion can be disconnected and the valve actuated to blow the mechanism essentially free of all product. The dispenser, along with refill units, can be purchased in hardware stores, lumber yards, and similar outlets.

The original form of the aspirator-type dispenser is the pump-sprayer for space spray insecticides. This normally consists of a tubular barrel (the cylinder) and a thin piston at the end of a fairly long rod, as shown in Figure 5.

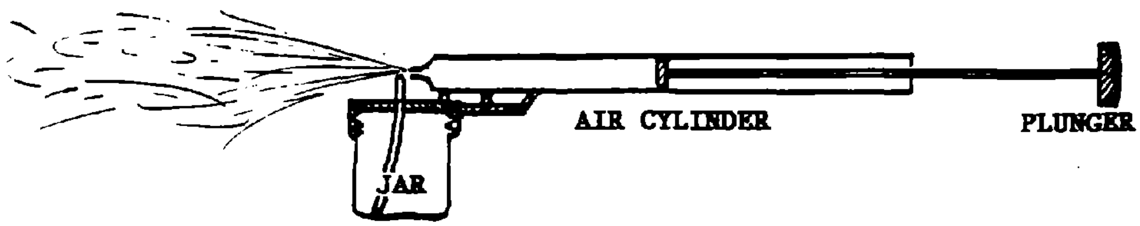


Figure 5. The "Flit Gun" Aspirator-Type Insecticide Space Sprayer

The product is aspirated up a plastic or metal dip tube and through a jet orifice that ends in the midst of a vigorous stream of air, at 10 to 20 psig (0.70 to 1.41 bar), directed at it from a nozzle at the end of the cylinder. The ratio of low-pressure air to amount of aspirated product is the primary determinant of particle size distribution. Ideally, the particle size would be less than 30μ. Otherwise, the larger particles would fall to the floor rather quickly and be of little use in killing houseflies, mosquitoes, and other flying insects. The largest-selling insect sprayers have been a line called "Quick Henry, the FLIT," sold by Penola Oil & Chemical Corporation, and later by Esso Oil Company, Humble Oil & Refining Co., and still more recently by Exxon, Inc.

These sprayers were often manufactured in very expensive forms, such as in nickel-plated bronze, with decorative designs and printing (sometimes engraved), and with small boxes of replacement piston "leathers" and spare glass jars that were often customized and suitably embossed with the name of the sprayer. Quart (946 mL) cans of insecticides in low-odor kerosene solvents were available from Penola, Esso, Sinclair, Phillips, Conoco, Shell, Peneco, Gulf, Pennsoil, Rex, Sohio, Cook, and other oil companies, which would work well in any of the available sprayers.

Today, a few firms make all-plastic sprayers, except for the metal orifice areas, but they are not advertised, and sales volume is limited. "F"-style or cone-top cans of insecticidal concentrates can also be found, but availability is also limited. These sprayers are far more popular in countries other than the U.S., Europe, and Japan.

The aspirator-type sprayers are the only sprayers, other than aerosols, that can produce a space spray. They have been so closely associated, however, with (smelly) insecticides that it would not be possible to market them for air fresheners or for other uses in the U.S. However, some "mini"-sprayers of this type are occasionally available for household perfumes in Latin America, and the rubber-bulb type aspirator may still be seen for personal fragrancing applications, generally in rather fancy designs. Colognes are available in bottles exceeding one U.S. gallon (3,786 mL) capacity for refilling other containers and dispensers, so a supply of the product itself is not a problem.

PUMP-SPRAYS - STANDARD TYPES

The Finger-Pump Sprayer

The most common pump sprayer is commonly called the finger-pump, mainly to distinguish it from the trigger-action sprayer. The finger pump is available from the same manufacturers that produce aerosol valves, such as the Calmar Corporation, Bakan Products Co., Risdon Manufacturing Co. (Division of CMP Products, Ltd., as of 1989), Emson Research Company, and others. The largest is probably the Seaquist Closures Division of Pittway, Inc., located in Cary, IL (U.S.). In many cases, it takes an expert to distinguish between a ferrule-type aerosol valve and a ferrule-type finger-pump valve; they are often made by the same company and have two or three components in common. Distinguishing features of the finger-action valve are its larger, more complex valve structure and its often clear plastic body component that displays a complicated spring above a metallic ball check unit. The best indicator is the type of container. If it is a plain glass bottle larger than one fluid ounce (29.57 mL), or a small glass bottle with flat surfaces or sharp corners, or a polyethylene or polypropylene or vinyl bottle, or if the bottle can be deformed by squeezing, or if the valve is attached by means of a screw-threaded connection, the valve is not an aerosol valve. Some finger-action valves are placed in one-inch aerosol cups and crimped onto aerosol cans. These defy identification except by operating them.

The usual aerosol valve has up to seven components and sells for about $40.00 per thousand. In contrast, the finger-action valve has eleven components, some of which must fit together with tolerances more demanding than those of aerosol counterparts. Consequently, these valves sell for two to three times the cost of the aerosol types, depending on size and other factors.

An illustrative sketch of a typical screw-cap mounted finger-action valve is shown in Figure 6.

The finger-action valve delivers a fixed amount of product per actuation, from 125 to 200 microliters. To convert this to milligrams per shot, simply multiply the microliter rating by the product density. Densities may vary by 20% or more. Ethanol solutions, such as hair sprays, have the lowest density, at about 0.80 g/mL.

As the actuator is depressed, the adapter and stem components are forced downward as well. The stem travels a fixed distance into the body chamber, which is normally filled with product in the primed valve. The product forces the piston to expand outward, allowing product to flow past it and into the cross-hole orifices of the stem. From there it travels up the stem hole, through the adapter and button, and out as a stream, or spray. When the button is released, the spring forces the stem upward, creating a partial vacuum in the chamber and causing the ball to lift and allow product to flow upward to refill the body chamber with the product.

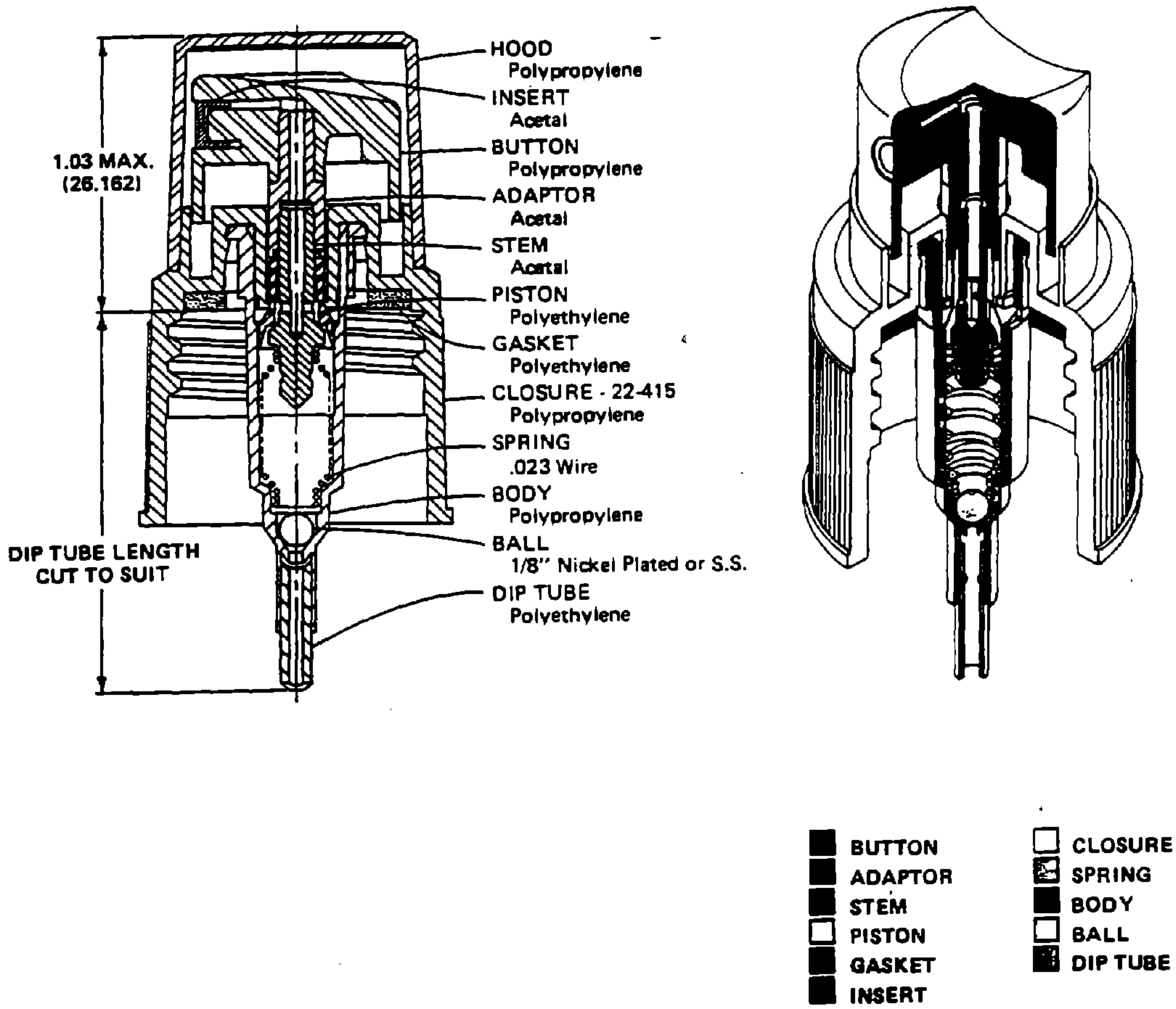


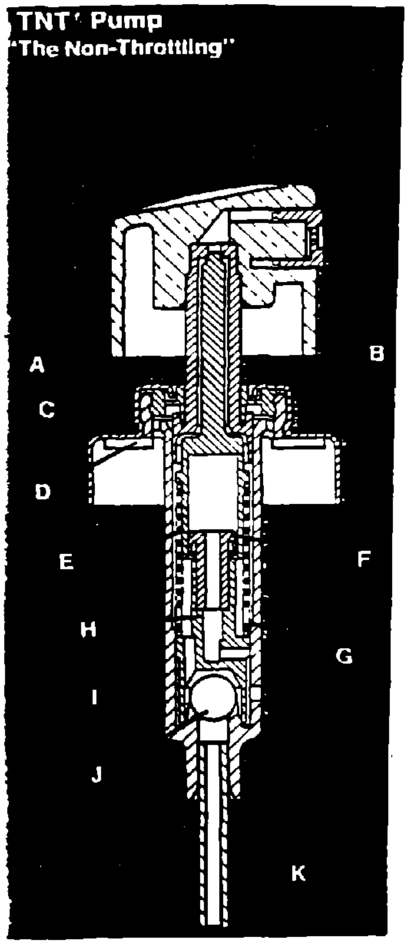
Figure 6. Cross-Section of Finger-Action Seaquist Valve, Set in 22-415 Closure

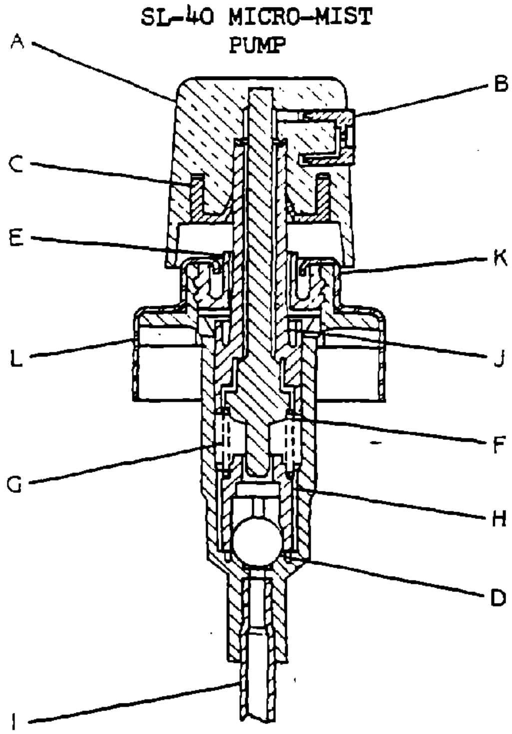
The complexity of the finger-pump valve systems makes them sensitive to strong solvents, solid suspension products and thixotropic viscous products. As a rule, they are only used for water-based, hydroalcoholic, and alcoholic formulations. The complexity of finger-pump valves is compared with the relative simplicity of a non-metering aerosol valve in the drawings presented in Figure 7. The complexity of the metering aerosol valve is more or less equivalent to that of the pump-action types.

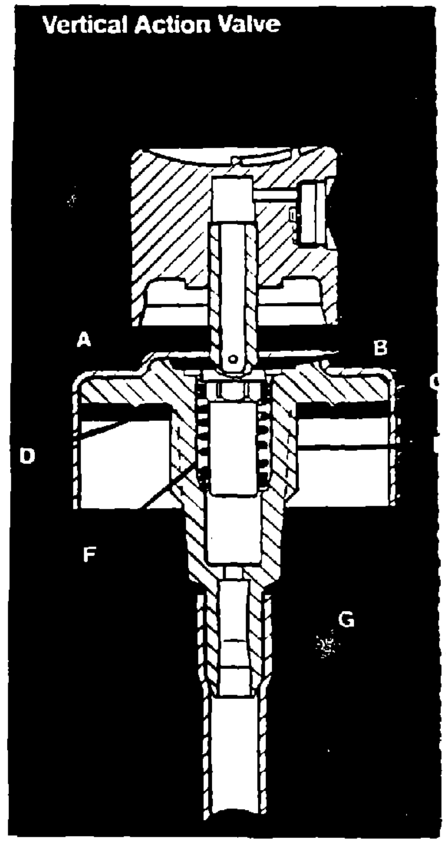
Along with the complexity of these valves comes a considerable increase in cost, compared with aerosol valve options. Costs may be controlled by using the largest practical containers (to lower cost per unit of product), by marketing refill containers that use simple screw-caps, and by emphasizing the use of finger-pump valves with colognes, sachets, perfumes, pharmaceutical, and other generally high-cost products. In the case of perfumes and some medicinal items, the metering action of the finger-pumps is a distinct advantage in conserving and regulating the use of these products.

The pressure build-up within the chamber of the finger-pump valve is a complex function of the pressure applied to the actuator, the size of the exit orifices (diameter mostly, but also length), product viscosity, and other factors, but it is generally in the order of 50 psig (3.5 bars). Mechanical breakup spray heads do a fairly good job of developing spray patterns when the liquid is at a pressure of about 18 psig (1.27 bar) or higher. At excessive pressures (rarely attainable) there is some denigration of the pattern, such as "hot spotting."

The spray pattern and particle size distribution of finger-pump sprays is due to the purely mechanical breakup attributes of the specially designed two-piece button. Two to four tangential channels converge the product into a central swirl chamber, where it must turn at right angles to pass through the terminal orifice.







MATERIALS AND COMPONENTS IN VARIOUS VALVES

A PISTON - Polyethylene	A ACTUATOR - Linear Polyethylene	A STEM - Nylon or Acetal
B COLLAR - Polyethylene	B ACTUATOR INSERT - Acetal	B STEM GASKET - Buna-N
C MOUNTING CUP - Alum.	C ACTUATOR ADAPTER - Polypropylene	C MOUNTING CUP - Aluminum
D GASKET - Rubber	D BALL - Stainless Steel #302 or #305	D BODY GASKET - Buna-N
E VALVE - Acetal	E COLLAR - Linear Polyethylene	E BODY - Nylon or Acetal
F INNER PISTON - P.E.	F BALL-SEAL INSERT - Acetal	F SPRING - SS-302
G SPRING - SS-302	G SPRING - SS-302	G DIP TUBE - Capillary PP with 0.020", 0.030" or 0.040" I.D., or 0.125" I.D. Polyethylene
H BODY INSERT - P.E.	H BODY & BODY INSERT - Polypropylene	
I BODY - Polypropylene	I DIP TUBE - Polypropylene	
J BALL - Stainless Steel	J PISTON - Linear Polyethylene	
K DIP TUBE - Polyprop.	K CLOSURE - Aluminum - anodized	
	L GASKET - Rubber of Polyethylene	

Figure 7. Comparison of Risdon (Dispensing Systems Division) Finger-Pump 20mm TNT Pump and SL-40 Micro-Mist vs. 20mm Aerosol Valve

Unlike most aerosols, where exploding actions caused by the instantaneous depressurization of liquified propellant act to reduce particle size to various degrees, the particle size of finger-pump sprays is regarded as very coarse, and best suited for surface applications. As a rule, spray particles from finger-pump units will strike the floor within five seconds or less, regardless of the initial direction of the spray. The only aerosols whose sprays compare with those of finger-pumps are "nitrosols," those pressurized with 1 to 6 grams of nitrogen gas (depending on size), and water-based types designed to have the hydrocarbon propellant separate on top as a discrete layer. Most of these latter products, such as starches and fabric finishes, carry a top-of-can message of "Shake Before Using" to obtain a better spray pattern by incorporating some propellant into the exiting product.

The finger-pump particle size distribution is compared with those of several similar products in Table 46.

Spray patterns of the finger-pumps vary from quite wide to very narrow. The valve of the "Moi•Stir" Mouth Moistener (Kingswood Laboratories, Inc.) will cast heavy droplets in a 7" (180-mm) slightly oval pattern onto a target panel 60" (1.51 m) distant. A "Hot Shot" Wasp & Hornet Spray (finger-action Calmar valve, ex. Bakan) by United Industries Corporation (St. Louis, MO), formerly Chemsico, Inc., will cast a narrow spray over 12 feet (4.35 m). Cologne sprays are usually the widest, with the particles traveling fairly slowly outward. In fact, cologne sprays, if deliberately ignited, will quickly burn back to the valve button and burn the fingertip of the operator, unless the spray shuts off first.

One of the detractions of the finger-action spray is the number of times the actuator must be depressed to empty the dispenser. For example, consider an 8.0-fluid ounce (299 mL) container, which is dispensed at the rate of 0.125 mL (125μL, or 100 mg) per shot. The required number of actuations to empty the dispenser will be 2,396. This number can be approximately halved by using finger-pump valves with 0.205 mL and similar size-metering dimensions. Many pump-spray marketers compensate for the slow use-up rate, compared with the

TABLE 46. AEROSOL AND FINGER-PUMP HAIR SPRAYS: COMPARISON OF PARTICLE SIZE DISTRIBUTIONS

Type & Valve	% of Propellants	Particle Size Range (μ)[a]			
		Below 10μ	10μ - 20μ	20μ - 50μ	Over 50μ
Finger-Pump mechanical breakup (MB)	0	0	2	14	86
Aerosol Non-MB	20	1	5	38	66
Aerosol MB	20	3	8	48	41
Aerosol Non-MB	25	2	8	49	41
Aerosol MB	25	5	15	60	20
Aerosol MB[b]	16.67	0.5	2	22.5	75
Aerosol MB[b]	32	16	18	39	27
Aerosol MB[b]	38	11	32	56	1
Aerosol Non-MB[b,c]	74	24	76	0	0

[a]Measurements made with a Malvern ST 1800 analyzer, at 90° to spray axis and 16" (406 mm) from the actuator. Run in duplicate.

[b]These are produced outside the U.S.

[c]The large amount of (CFC-11/12) propellant used in this product reflects the high cost of ethanol in the country where it is produced; the "alcohol tax" cannot be avoided, as in the U.S., for approved uses.

aerosol, by increasing the level of film-forming resin in the hair product formulation.

Some characteristics of pump-sprays are more economically attractive than aerosols. For example, a plain glass cologne bottle, is less costly than a heavier-walled, pressure-tested and PVC "Lamisol"-coated glass-in-plastic aerosol bottle. The plain bottle also has a number of other advantages relating to design flexibility. The filling operation for pumps is a single stage operation; the aerosols, however, must be filled and then gassed, requiring at least two stages. They must also be hot-tanked.

Aerosol containers larger than 4 fluid ounces (118.3 mL) are restricted to cylinders of aluminum or steel, at least in the U.S.; whereas, finger-pump dispensers may be made of various plastic or glass containers and be attractively shaped. Unlike aerosols, they are not limited to 819.4 mL in size, although very few are more than about 12 fluid ounces (355 mL), for practical reasons.

The flammability of aerosols and finger-pumps is commensurate in several ways. Formulas for both systems may range from 0% to 100% of flammable components. They pose approximately equal levels of hazard if exposed to an ongoing fire in a warehouse. The finger-pump can produce a flame volume of from 0.8 to 1.6 U.S. Gallons (3,000 to 6,000 mL) per actuation if the contents are hair spray or bug killer, which contain essentially 100% flammable ingredients. The aerosol is similar, but the flame volume may be two or three times larger and may be sustained by merely keeping the button depressed. Aerosols can rupture if overheated, and if a flame source is present, they may generate a fireball up to 9 feet (2.7 m) in diameter.

Typical products that have been successfully marketed in finger-pump sprayers include following:

Bug Killers (such as ant, roach, spider, and bee killers)
Weed Killers
Pet Sprays (often for insecticidal or grooming purposes)

Colognes and Perfumes

Hair Sprays

Hair Moisturizers

Curl Activators

Lens Cleaners (such as anti-fog and anti-static types)

Vermouth (for dry martinis)

Germicides (including those for pre-operation washing)

Spot Cleaners

Pre-suntanning Accelerator

Facial Rinse

Cookware Lubricant

Contact Lens Rinsing Sprays (requires Thimerisol or other disinfectant)

Window Cleaners

Topical Sprays (such as benzocaine or rubifacient types)

Silver Polish Sprays

Throat Sprays

Leaf Shine Sprays

Chrome Polishing Sprays (automotive uses)

Stainless Steel Cleaners

Mildewcides

One disadvantage of finger-sprays not yet discussed is that all models to varying degrees produce extremely coarse dribbles at the very beginning and the very end of each actuation. These heavy droplets fall downward very fast, spotting polished wood furniture, window sills, flat glass surfaces and some textiles, also cooling or wetting the skin away from the sprayed area of the body.

Finger-pump sprays are usually not used with a number of product types such as the following:

Volatile flammables	(such as cigarette lighter fluids)
Viscous liquids	(spray extra coarse, or may not spray)

Strong solvents	(such as nail polish removers & insect repellents)
Sterile liquids	(sterility is lost at the first actuation)
Acidic liquids	(acetal valve components dissolve below pH = 3.6)
Moisture-sensitive liquids	(moisture enters by return air and permeation)
Suspensoid fluids	(valve plugging can readily occur)
Foam-type emulsions	(foaming will not occur to any extent)
Polyethylene warping liquids	(such as oleic acid or some block polymers)
Staining liquids	(such as food colors, dyes, etc. because of dribble)
Sensitive liquids	(such as those harmed by air or light)
Two-phased liquids	(phases will reform in valve chamber and be resistant to reconstitution by shaking)
High-odor liquids (In plastic bottles)	(garlic concentrates, etc. will permeate)

In spite of all these apparent limitations, the finger-pump sprays enjoy a business volume exceeding one billion units a year and remain the major competitor to aerosols.

Trigger-Pump Sprayers

The sprayer is one form of the trigger-pump; the others extrude pastes, gels, or liquid products. Trigger-pump sprayers are more costly than finger-pump sprayers; they are used with somewhat larger dispensers, and more emphasis is given to refill units. The trigger mechanism facilitates the dispensing of larger quantities of product per shot, and the mechanical advantage or leverage feature of the pinioned trigger itself provides higher internal pressure in the chamber. They are generally viewed as more utilitarian than discretionary; for example, there are few if any trigger type pump-action hair sprays. (However, trigger pump lotions and cosmetic pastes are aesthetic and quite popular.)

Most trigger sprays are used for cleaning purposes, such as pre-laundry spot cleaners, disinfectant cleaners for hard surfaces, carpet cleaners, window cleaners, automotive cleaner and wax, vinyl top cleaners, industrial lubricant cleaners, and concrete floor (grease and oil) cleaners. Container sizes of up to one U.S. Gallon (3,784 mL) are available for institutional uses.

The operational principles, compatibility characteristics, and most other properties of the trigger-pump sprayers are equivalent to those of the smaller finger-pump sprayers and need not be repeated here.

Finger-Pump Extruders

A minor modification of the actuator changes the finger-pump sprayer into an extruder suitable for dispensing lotions, creams ointments, gels, pastes, viscous liquids, and measured amounts of various concentrates for dilution with fixed amounts of water. The actuator is removed and replaced with a spout with a very narrow tubular exit pipe. The small amount discharged per shot makes it useful for costly pharmaceutical, skin dewrinklers, perfumed lotions and similar products. In Europe, a vitamin mixture and an ear-wax softener are sold in this form. A concentrated cypermethrin and K-methrin mixture that is dripped onto an absorbent wafer measuring about 17 X 45 X 2 mm in size is also sold in this form. The treated wafer is slipped into a small holder that plugs into a wall socket which gently heats it to vaporize the insecticidal additives. The active ingredients are not volatilized in sufficient concentrations to be lethal, but they are so irritating to mosquitoes that they vacate the room if possible. The repellent action lasts 8 to 10 hours, ensuring people a good night's sleep. Most of the sales are in Mediterranean countries, where the product has made serious inroads into the much more costly aerosol insecticide business.

Trigger-Pump Extruders

Various modifications can be made to the trigger-pump sprayer to change it to a device with a spout able to dispense lotions, gels, and similar products in the form of a stream or ribbon. Simplified and lower-cost versions are also in demand that are used to discharge relatively large, fixed volumes of dishwashing detergents, fabric softeners, and other cleaners. They will have almost no effect on the aerosol market as possible alternatives and are not discussed further.

DISPENSING CLOSURES

One of the simplest possible designs is the screw-threaded closure or cap with a dispensing hole able to be plugged shut by various means. Three of these designs are illustrated in Figure 8.

To operate these, the dispenser is held inverted to get the product near the orifice, after which, the "F"-style metal can (oblong, with large front and back flat surfaces) or flexible plastic container is squeezed, expelling a stream or ribbon of the product. Dispensers come in sizes of 6 to 64 fluid ounces (177 to 1,892 mL) and can conveniently dispense liquids, thin gels, soft creams, and lotions, as long as they are flowable. These containers are used for charcoal lighters, various cosmetics, toiletries, personal care products, paint solvents, paint strippers and furniture polishes.

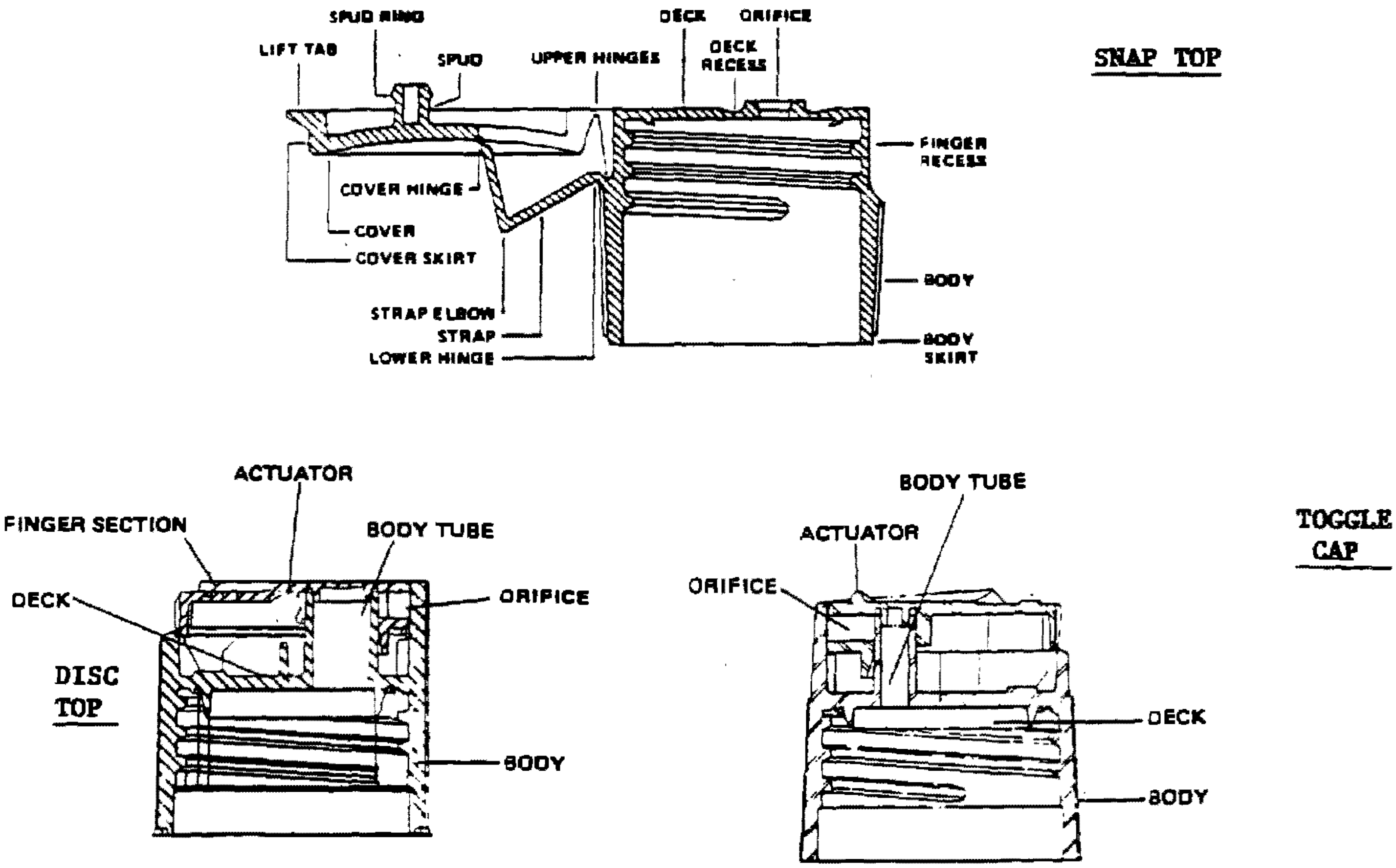


Figure 8. Various Dispensing Closures-Made by the Seaquist Closures Division

In addition to the designs illustrated above, there are turret spouts (truncated cone profile), lever spouts--in which a small pinioned plastic section is rotated 90° upward to operate the closure--and several related forms. They are increasingly used instead of the simple, detachable screw-cap dispensers. Uses include certain foods (such as oleomargarine pourables, ketchup, and mustard), lubricants, silicone shoe and boot dressing, some medicinals, and solvents for home use, artists, and industry.

These products are major competitors with aerosols in the lubricant field (aerosol volume 95,000,000 units in 1988), for carburetor and choke cleaners (aerosols 57,000,000), waxes and polishes (aerosols 129,000,000), and certain other overlap product areas. Since the closure is a single polyethylene molded unit, generally applied semi-automatically as a replacement for screw-threads, it is a very economical option. Some models can be made child resistant.

PRESSURIZING DISPENSERS

Twist-N-Mist II

Over the years, several firms have developed various pressurized packaging systems quite different from the conventional aerosol form. They invariably use air pressure, the restorative pressure from an expanded rubber bladder, or some similar arrangement as the dispensing method. They are characterized by delivering either very coarse sprays or various lotions and semi-solid products, usually one or the other.

The Twist-N-Mist II is a development of the CIDCO Group, Inc. of Denver, CO, which holds several U.S. Patents that cover the principles of the device, as well as those employed in related dispensers: Pull-N-Mist and Dial-A-Spray, details of which are still experimental and have not yet been released. The firm also holds several foreign patents.

As in all such products, energy must be imparted to the dispenser to take the place of the propellant gases used in aerosol forms. For Twist-N-Mist II, that energy is supplied manually, by rotating the full-diameter screw-cap and integral piston.

The current model of Twist-N-Mist II, of which several hundred have been made, uses a three-component outer shell assembly, which measures about 2 3/4" X 6 1/2" (70 X 165 mm) and consists of an HDPE threaded base, threaded top, and matching body, as shown in Figure 9.

By turning (twisting) the threaded cap several revolutions the integral piston in the base of the cap is raised about 1/2 inch (12.7 mm) or so, creating a vacuum in the cylinder (reservoir) below. This causes the product to rise up the dip tube, past the stainless steel ball check valve, to fill the cavity. Enough is drawn up to provide a 7- to 20-second spray time, depending on the valve orifice.

The cap is now twisted an equal number of turns in the opposite direction, forcing the integral piston downward until it hits against the base of the reservoir. This action causes pressure to develop in the reservoir and forces the trapped product downward into a Buna-N rubber bladder, which expands accordingly. The memory of the elastomer causes pressure, which decreases to some extent as the product is dispensed through an aerosol type valve, allowing the bladder to slowly regain its original "test-tube-like" profile. The process must be repeated for another actuation. The dimensional changes in the unit during the suction and pressurization stages are shown in Figure 10.

As a fail-safe feature, the contents of the pressurized rubber bladder will very slowly bleed back past the check valve barrier and into the main product storage compartment. The bleed-back time can be controlled by varying the surface finish of the check ball or check ball receptacle, or, if the product is viscous, by grooving the ball.

A number of other features are possible. The amount of pressurized product (and thus spray time) can be pre-engineering by proper sizing of the reservoir, bladder and/or nozzle orifice. The main section of the dispenser,

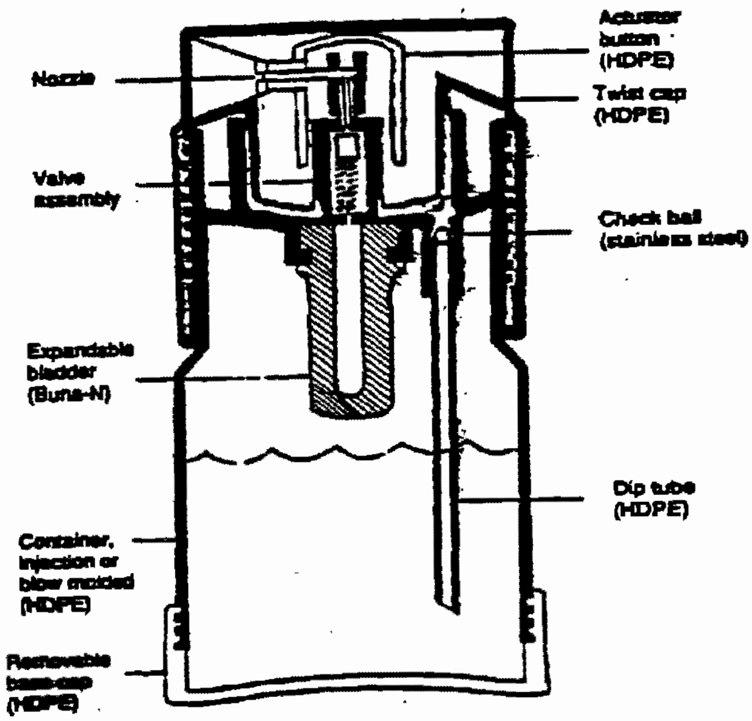
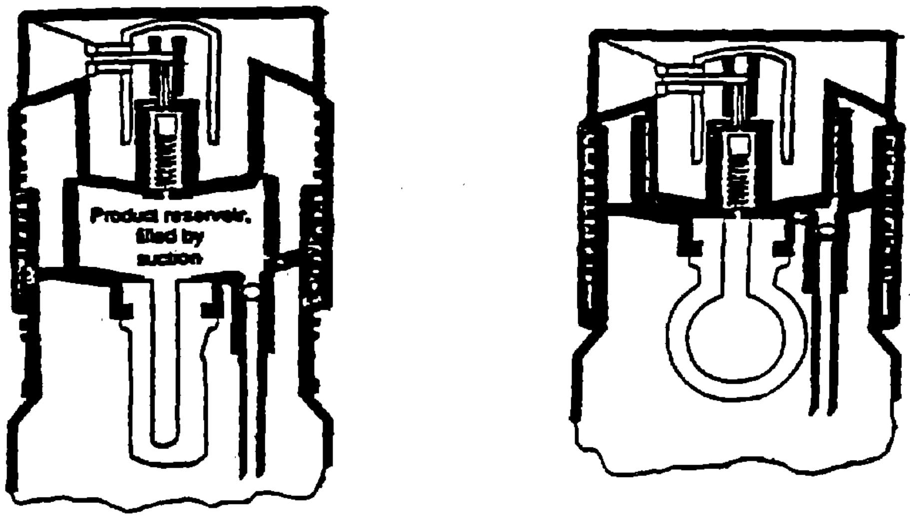


Figure 9. Twist-N-Mist II



FILLING RESERVOIR Turning cap to the up position opens the reservoir and fills it through suction on the dip tube.

DISPENSING SEQUENCE Twisting cap back to the down position forces the product from reservoir to bladder. Pressing actuator discharges contents.

Figure 10. Suction and Pressurization Stages of the Twist-N-Mist II Dispenser

made from injecting blow-molded HDPE or HDPP, can be contoured to a modest degree inward, outward, or both, if the screw-threaded top and bottom sections remain round. Technically, the dispenser can be provided with an integral bottom at a slight decrease in cost, but this would make it into a one-time service unit, instead of a reusable type and increase cost-per-ounce (cost per mL) significantly. This option is not generally recommended.

Because the upper cavities are completely filled with product, the unit may be used with the dispenser held in any direction. It delivers about 95+% of the contents. Corrosion is not a problem, since the only metal parts are a stainless steel spring and ball. Stress cracking has been noted as a problem with early single cavity models, mainly affecting the screw-threaded dome section and allowing leakage of the product. If refined models are resistant to stress cracking, they should be tested with surfactant (as non-ionic) water solutions that can often induce this problem in polyethylenes that are not formulated properly.

The CIDCO Group, Inc. recites the shortcomings of aerosols (their major target) as well as of finger-pumps and trigger-pumps, claiming that their dispenser, while somewhat costly to buy the first time, has long-range advantages, especially if refilled.

However, several turns may be necessary to pull product from the main chamber and then force it into the Buna-N Rubber bladder against the back pressure from that diaphragm. The spray duration could cease in the middle of a spray episode, requiring the user to delay completion for an estimated 15 to 30 seconds to recharge the can. The spray is much coarser than that of aerosol sprays, except for nitrosols. No foams can be produced. No solvents that have a profound swelling or deleterious effect upon the Buna-N bladder can be used, except perhaps at low concentrations. Product darkness or odors may develop unless the rubber bladder is specially lined, as in the Exxel system discussed below.

The Exxel System

Briefly, this is another dispenser option where the product is contained in a thick, squeezable rubber sleeve open at one end, but in this case all the product is compressed into the inner container by a manufacturer or packager. The dispenser has aerosol properties, in that the product is always under pressure. However, there are differences. Sprays are propellant-free, and therefore very coarse or wet, and no foam type products can be provided except for post-foaming gel types.

The following steps are required to manufacture the Exxel System dispenser:

- Stretch-blow a biaxially oriented, thin-walled polyethylene teraphthalate (PET) bottle;
- Form longitudinal pleats in the bottle, using patented equipment;
- Apply a double layer of barrier sealant and liquid latex to the bottle;
- Insert a customized valve and clinch in place at the top ring of the bottle;
- Insert bottle into a rubber sleeve;
- Place container into a suitable outer container and attach at the top; and
- Force a predetermined amount of product into inner container via the valve.

Construction materials that can contact products are limited to the PET bottle, the Nylon 66 valve housing, natural polypropylene, the HDPE button, and either the SS #302 or #316 spring. An insignificant exposure to the PET/valve gasket must be mentioned. The gasket is available in various materials.

A sampling of products currently being packed in the Exxel system appears in Table 47.

Exxel comments that skin care, hair care, and pharmaceutical products of the post-forming gel type are well along in the development stages. Also, several medicinal ointments are under intensive study by Upjohn and others. Cost comparisons can be made with other forms of packaging, using the tabulated data in Table 48.

The Exxel system is incompatible, to varying degrees, with certain formulations. Following is a list of ingredients and characteristics that would make a product incompatible with the Exxel system:

- Certain polymer solvents--terpenes, ketones, etc.;
- pH Values over 10.0;
- Isopropanol, above 5.0%;
- Prolonged exposures to over 113°F (45°C);
- Particulate matter--since effective shake-before-use is impossible;
- High surface tension breakup products;
- Resins with an ability to dry and clog actuators;

TABLE 47. TYPICAL CURRENT CUSTOMERS AND PRODUCTS OF THE EXXEL SYSTEM

Company	Product
Air Products and Chemicals Company	Welding Flux Spray
Chanel, Inc.	Sun Oil Spary
Kobayashi Pharmaceuticals Company	Muscle Relaxant
Nihon Sanso, Ltd.	Pure Food Products - sterile
Prudue Frederich, Inc.	"Betadyne" Solution[a]
P.R. Hertensen	"Citruscent" Fragrance
Tokyo Aerosol Co.	Hair Gel
Wella	Shampoo and Conditioner
Jergens	Topical Lotions[b]
Westwood Pharmaceuticals, Inc.	"Alpha Keri" Spray Oil
Adrien Arpel	"Aromafleur" Flower Extract Foam Firming Masque
Estee Lauder, Ltd.	Hair Reviving Mist
HiLo Products	"Silent Force" Flea Spray
Laboratoires Goëmar, S.A. (France)	"Tonialg" Restorative Conditioner "Tonialg" Toning Lotion "Tonialg" Night Creme "Tonialg" Restorative Shampoo "Tonialg" Hand & Body Creme "Tonialg" Bath & Shower Gel "Tonialg" Foaming Bath "Tonialg" Cleanser "Tonialg" Nourishing Creme "Tonialg" Body Contouring Creme

[a]Tamed Iodine formulation.

[b]As of 1988.

TABLE 48. COST OF EXXEL SYSTEM PACKAGING AND FILLING SERVICES (VOLUME = 1MM)

Item	4 oz. ($/M)	7 oz. ($/M)
Snap Ring	16	16
Power Assembly Unit	241	274
Actuator	30	30
Overcap	22	22
Decorated Bottle	85	95
Filling Charge (Contract)	140	140
	534	577

NOTE: Add $10M for 500,000 quantities and $20M for 250,000 quantities.

Add $25/M for pre-fill electron beam sterilization.

- Formulas that require in-package mixing, e.g., bi-phasics; and

- Ethanol, above 60%--should be carefully tested for compatibility.

The outer container may be made from glass, plastic metal, composites, paper, or (theoretically) nothing at all. For automated filling, the container should be able to support a hold-down filling force of 25 pounds (11.4 kg) without buckling. To accommodate the two Exxel System inner containers, the minimum internal dimensions of the outer containers must be considered, as shown in Table 49.

The smaller (4-fl.oz.) Exxel package will deliver 92 to 95% of its contents before fully depressurizing. The 7-fl.oz. size will deliver 92 to 84.7%. These ranges are reduced to 90 to 93% in the case of fairly viscous items with positive yield points. After about 86 to 88% of spray products have been dispensed, the bag pressure falls below about 17.5 psig (1.23 bar) and the spray pattern deteriorates rapidly. The pressure at which this occurs depends on the ingredients and the viscosity of the formulation. As a rule, storage weight loss will be 1.0% per year at ambient temperature or per month at 104°F (40°C).

The Exxel System is self-pressurized and may be classed as an aerosol under the DOT shipping regulations; however, DOT Exemption No. E-9607 has been obtained by the Darworth Company (Div. of Ensign-Bickford, Inc.) to set aside these requirements for hot tanking, etc. This now applies to all Exxel System products.

<u>The Mistlon System</u>

The Mistlon Eco-Logical Spray Bottle is a dispenser developed in Japan, made in South Korea, and offered for sale by the MONDEX Trade & Development Corporation, 2 St. Clair Avenue - West (Suite 801), Toronto M4V 1L5, Canada. It is cylindrical and measures 2 1/8" X 8 1/2" high (54 X 216 mm). The wholesale price is about $1.00.

TABLE 49. MINIMUM DIMENSIONS OF OUTER CONTAINERS FOR EXXEL UNITS

Dimension	4 oz. Size	7 oz. Size
Minimum length. Top of neck finish to inside of bottom.	5.450 in. (138 mm)	7.300 in. (185 mm)
Minimum width. Internal dimension.	2.223 in. (56.5 mm)	2.223 in. (56.5 mm)

Note: Intentionally underfilled Exxel units will permit the use of outer containers with reduced minimum internal widths.

Outer containers require a vent hole of at least 0.015" (0.38 mm), preferably in the base, but alternatively in the shoulder.

To use the empty unit, the full-diameter polypropylene cap is removed, after which a screw-threaded closure carrying an ordinary aerosol valve and actuator is also removed. A quantity of product is poured into the bottle through the one-inch (25.4 mm) opening. A typical fill is 250 mL. After this, the closure is screwed back into place, allowing a thin rubber "O"-ring to make a reliable hermetic seal. The base section [full-diameter and 1" high (25.4 mm)] is now withdrawn, away from the rest of the unit, exposing a hollow cylinder 11/16" in diameter by 3 11/16" long (17.5 X 93.7 mm), fitted with a one-way compound valve. The hollow cylinder functions as a piston, within a cylinder protruding upward into the container, also ending in a one-way valve. To pressurize the air in the container, the base section is pumped a number of times. By pressing a soft diaphragm in the center of the base, excess air pressure within the hollow cylinder is removed, allowing it to fit snugly against the bottom-most area of the body as before.

The unit is equipped with either a 0.010" (0.25 mm) or 0.014" (0.36 mm) mechanical breakup bottom. In the case of water, these actuators will provide an acceptable spray if the air pressure is 18 psig (1.17 bar) or greater. The operating characteristics follow simple gas laws. This can be illustrated by the following example.

Characteristics:

The head space volume is 100 mL.
The liquid volume is immaterial.
The applied pressure is 50 psig (3.52 bar).

Question:

How much product can be dispensed before the pressure sinks to 18 psig (1.17 bar) and the spray starts to deteriorate?

Solution:

Convert to absolute pressures.

50 psig = 64.7 psi-abs (4.56 bars - absolute)

18 psig = 32.7 psi-abs (2.30 bars - absolute)

Boyle's Law:

$$V_2 = V\ (P\ /P_2) = 100\ mL\ X\ (64.7/32.7)$$

$$V_2 = 197.9\ mL$$

Change in head space volume.

$$V_o = V_2 - V = 197.9 - 100.0 = 97.9\ mL.$$

Answer:

97.9 mL of liquid can be dispensed before the spray deteriorates.

It follows that, the larger the head space, the more strokes of the piston will be needed to pressurize to a given level, and the more liquid can be dispensed as a result.

With some degree of manual difficulty, the Mistlon unit can be pressurized to 65 psig (4.58 bars). There was no evidence of deformation at this pressure. The unit might be pressurizable to well over 100 psig (7.04 bars) without any problems unless it is strongly heated to the point where the polypropylene begins to soften and become deformable.

The delivery rate will, of course, vary with the container pressure. With the 0.014" (0.36-mm) MB valve button, water delivers at about 0.5 g/s at 20 psig (1.41 bar) and about 0.72 g/s at 40 psig (2.82 bar).

Like the Twist-N-Mist dispenser, the unit is limited in terms of spray particle size and range of products that can be dispensed. Highly flammable materials, those that deform polypropylene or attack polyvinylacetate, and viscous fluids are among those that should not be used. The unit cannot be used to generate a direct foam, but with a suitable straight bore actuator it could direct a thin stream into the palm that would then spring into a foam.

Airspray

This product, which is similar to the Mistlon dispenser also uses a pumping action to compress air into the pressure-resistant container. When reasonably full, it must be pumped 10 to 20 times to create an effective spray that does not quickly deteriorate as pressure drops. As the container empties, the number of pumping strokes must be increased, but the pressure lasts longer during dispensing. The unit must be held upright to keep the diptube below the liquid surface, but if the container is held so that the compressed air is unloaded, it can be quickly pumped up again, unlike aerosol products with nitrogen or other propellants in low concentrations.

The cylinder is cylindrical to withstand the generated air pressures without buckling or other deformations. Comments made about the Mistlon dispenser apply here as well.

Invented in Sweden, the Airspray system was developed and refined by a Dutch company, which marketed the unit in Europe for several years. In 1987 they entered into an agreement with the National Can Corporation, which is now a part of the American National Can Company unit of Pechiney, S.A., to manufacture and market the system in the U.S. under license. As of 1989, the system will be jointly marketed in the U.S. by Airspray International, Inc. (Pompano Beach, FL) and American National Can Company (Chicago, IL). It is promoted in Canada by W. Braun & Company (Markham, Ontario L3R 3B3, Canada).

The system is offered in two versions: with a refillable screw top and a disposable crimp-on. It can be made in containers of plastic, metal, or glass. PET containers are being developed at this time. All the parts are plastic. Once pressurized to 55 psig (3.87 bars)--the recommended maximum--it will dispense up to 100 mL before repumping is needed. Airspray supplies an

O.T.I. crimping machine for closing and pressurizing the system at 1500 μ/hr with compressed air.

The Werding Nature Spray-Systems

A variety of inter-related systems have been developed by Werdi Spray, S.A. 5, Route des Jeunes, CH-1227 Geneva (Switzerland). They are represented in the U.S. by Werding Aerosol Technology Inc., U.S., located at 4978 Kingsway, Burnaby, British Columbia V5H 2E4, Canada.

The firm makes both non-aerosol containers and their unique Werdi 'R' Actuator. The latter can be designed to provide a constant delivery rate, regardless of the internal pressure of the dispenser, and is thus most useful for products pressurized with air, nitrogen, carbon dioxide, etc., where pressure drops during use can exceed 70%. The Werdi 'R' System comprises the Werdi 'R' Actuator (fitted with the Werdi 'N' Nozzle and thrust regulator) and the Werdi Valve. For lotions and creams, the Werdi 'RD' system is suggested, which consists of the Werdi 'RD' Actuator (fitted with the thrust regulator and a self-closing diffusor) and the Werdi Valve.

The Werdi 'N' Nozzle achieves a high mechanical breakup effect by means of its multi-staged, interconnected Venturi system, and thus contributes more to spray breakup than conventional (less costly) mechanical breakup actuators. Fitted behind the nozzle in the actuator, the thrust regulator controls the flow of product to the nozzle. The patented design includes two stainless steel accelerator discs and a plastic expansion chamber as well as a special regulation disc, which is cut, curved, and formed to exacting standards.

The regulation disc is compressed by higher pressures, but because of the spring effect of the metal, this opens the cut and increases the orifice size as the pressure drops. Turbulence intentionally created by the design of the companion discs, as well as the nozzle itself, produces a resistance to the product flow into the thrust regulator, whose force is directly proportional to the pressure. The higher the pressure, the more these turbulent effects brake the delivery rate. Thus, the Werdi 'R' Actuator maintains a constant outflow of product from the container.

There are four types of the Werdi 'N' Nozzle, which are used for different spray rates and patterns. When a nonaerosol (or aerosol) container is filled to 65 volume percent with low-viscosity concentrate and then pressurized with air or nitrogen to 85 psig (6 bars), the results are as shown in Table 50.

Werdi also makes complete valves as well as nonaerosol (pump-type) containers, but their primary contribution to nonaerosol dispenser technology appears to be in the actuator area. The following U.S. Patents are reference sources: 4,487,554 (11-DEC-84), 4,260,110 (7-APR-81), and Battelle's 4,603,794 (5 AUG-86). The last describes a dispenser able to deliver a high-pressure spray by means of a low-pressure squeeze on the flexible sidewall area, following a pressure multiplying principle.

Latest reports suggest that a large Northern Italian watchmaking firm is interested in purchasing Werdi because they have facilities to produce many of the very small actuator and other parts required for the system.

MISCELLANEOUS AEROSOL ALTERNATIVES

A number of dispensers can be used to present products that compete with the aerosol system, although they may bear no direct similarity to aerosols. Two will be considered in the following pages.

Insecticide Vaporizers

Vaporizers of various types have been used to provide "true aerosol" mists or condensation nuclei of products in the air. For the most part, they have been used for insecticides, but triethylene glycol mists of hexylresorcinol and other health-related products have enjoyed a much smaller market.

TABLE 50. SPECIFICATIONS--USING FOUR NOZZLES--FOR THE WERDI 'R' ACTUATOR

Nozzle	Type A	Type B	Type C	Type D
Color Code	White	Yellow	Green	Black
Average Delivery Rate (mL/sec.)	0.70	0.47	1.30	1.30
Average particle Size (microns)	3[a]	5[a]	0.7 - 3[a]	25 - 50
Cone Angle of Spray Pattern	50°	30°	40°	30°
Cone Length (inches)	30	24	55	36
Range of Applications	Personal Deodorants	Hair Spray	Space Insecticide	Polishes
	Pre-shaves	Wound Spray	Air Fresheners	Surface Insecticide
	Leaf Polish			Surface Disinfectants
	Mold Releases			

[a]The average particle size for Types A, B, and C appear to be unusually low for air sprays.

In Latin America, Spain, Portugal, Tripoli, and other areas the electrically vaporized insecticide products form the largest single use for insecticide applications. Individual insecticide wafer sales volumes are greater than the total aerosol markets in these countries. Such well-known firms as S.C. Johnson & Son, Inc., Refinacoes de Milho, Brasil, Ltda (STP Brands), Bayer, GmbH (BAYGON Brands), and Reckett & Coleman, Ltd. (Various Brands) sell the wafers.

The wafer, which contains a few drops of absorbed insecticide concentrate, is placed in a holder on the heater, which is then connected to a wall plug of electric current. The wafer is gently warmed to release the insecticide materials. Although nontoxic at low levels of use, the insecticides irritate mosquitoes (and "permilongos"--long-legged mosquitoes) so that they leave the room. Especially useful in sleeping quarters, the wafer has useful service life of from eight to ten hours. Foil packs of these products are now being replaced with PET-laminate packs to reduce packaging costs.

Stick Products

Coming into major use only about ten years ago, the stick-in-canister option has become the leading alternative for antiperspirants and personal deodorants. A much smaller market exists for other items such as stick insect repellents, stick spot-cleaners for textiles, stick analgesics (methyl salicylate types, for example), and several other products.

Several types of polyethylene and polypropylene round and oval canisters exist. The most popular are in the 1.5- to 3.5- Av.oz. (42.5 to 99.2 g) size, with a bottom-entering plastic screw that, when rotated, elevates the product so that it protrudes sufficiently from the top of the canister to allow for convenient use.

A typical stick antiperspirant formulation contains 20 to 25% of the aluminum chlorohydrate complex salt, compared with 7 to 12.5% in aerosol products. Two representative formulas appear in Table 51.

TABLE 51. TWO STICK ANTIPERSPIRANT FORMULAS

Antiperspirant Stick

Ingredient/CTFA Name	%
Phase A	
Permethyl 99A[a] Isododecane	17.15
Permethyl 101A[a] Isohexadecane	4.00
Dow Corning 244[b] Cyclomethicone	13.15
Fluid A/P[c] PPG-14 Butyl Ether	11.50
Phase B	
Crodacol S-95[c] Stearyl Alcohol	11.50
Castorwax MP-80[d] Hydrogenated Castor Oil	7.50
Phase C	
Micro-Ace P-2[a] Talc	10.50
Phase D	
Spheron P-1500[a] Silica	2.00
Phase E	
Micro Dry[e] Aluminum Chlorohydrate	22.00

Manufacturing Procedure: Add Phase A in order to vessel, heat to 70-75°C. Mix until clear and uniform. While mixing, add Phase B one item at a time. Continue mixing until clear and uniform. Maintain 70 to 75°C, add Phase C, keep agitation vigorous. Add Phase D, mix for 5-10 minutes. Pour into containers at 66-68°C.

Improved Antiperspirant Stick Formula

Ingredient/CTFA Name	%
(A) Cyclimethicone	43.5
Stearyl Alcohol	23.0
PPG-15 Stearyl Ether (ARLAMOL E) (ICI Specialty Chemicals)	5.0
(B) Hydrogenated Castor Oil	2.0
Steareth-20 (BRIJ 78) (ICI Specialty Chemicals)	1.0
(C) Silica	0.5
Aluminum Chlorohydrate	25.0

Procedure: Heat (B) to approximately 65°C until liquid. Add (A) with moderate agitation and heat to minimize silicone evaporation. Add (C) and stir 5-10 minutes until uniform. Cool to 55°C with stirring and pour into stick forms.

Suppliers:
[a]Presperse Inc.
[b]Dow Corning
[c]Croda
[d]Cas Chem
[e]Reheis

All significant marketers of aerosol underarm products also sell the stick products. Each line generally has two sizes and "scented" and "unscented" versions. Product effectiveness is equivalent to, or somewhat higher than, those of the latest generation of aerosols, and the "anti-perspirancy" of both versions is well above FDA requirements.

The antiperspirant type of underarm product commands 81% of the total underarm aerosol business, and 83% of the stick alternative. The personal deodorant subsegment is presented in the same container types and sizes. Instead of aluminum astringent salt, it contains 0.1 to 0.2% of a germicidal material, typically Triclosan, a diphenyl derivative made by Ciba-Geigy Corporation. Table 52 shows approximate production volumes of aerosol and stick underarm products.

Other packaging forms, including roll-ons and pads, make up a relatively minor proportion of the U.S. market. These secondary alternates will not be covered here.

Aerosol and stick underarm products are mature markets. The change in ratio shown in Table 52 is the result of new antiperspirant entrants (Bristol-Myers and Mennen) whose advertising helped both their products and the aerosol packaging concept. In addition, reformulation to more powerful forms of the aluminum chlorohydrate have made aerosol antiperspirants more effective. Unless significant changes in price structure, ecological aspects, flammability considerations, or other criteria affect one product at the expense of the other, the 1:1.50 ratio of aerosols to sticks will probably continue for a long time. No dramatic changes are seen in this ratio for at least four years.

TABLE 52. PRODUCTION UNITS OF UNDERARM PRODUCTS (U.S.)

Year	Aerosols	Sticks	Ratio
1986	153,000,000	258,000,000	1:1.69
1987	164,500,000	278,000,000	1:1.69
1988	193,000,000	292,000,000	1:1.51
1989[a]	207,000,000	310,000,000	1:1.49

[a]Estimated figures at mid-1989.

SECTION 3

SUMMARY

Part I of this report discusses the aerosol industry's experience in converting from CFC propellants to alternative aerosol formulations. Some of the immediately available alternatives, such as HCFC-22 and 1,1,1-trichloroethane, also can deplete stratospheric ozone levels, although their ozone depletion potentials are less than those of the CFC propellants.

Such compounds as HCFC-123, HCFC-124, HFC-125, HCFC-132b, HCFC-133a, HFC-134a, and HCFC-141b are now undergoing extensive toxicological testing that will continue until about 1992. Many of these "future alternative" compounds are nonflammable unless they are mixed with substances such as iso-butane or ethanol; others are flammable. Hydrocarbon propellants, which cost less than CFCs, are often the propellants of choice unless special properties such as increased solvency or reduced flammability are needed. Dimethyl ether (DME) is the next most preferred CFC alternative. DME is flammable and a strong solvent.

Carbon dioxide, nitrous oxide, and nitrogen are inexpensive and widely available throughout the world but have been underused as aerosol propellants. Special equipment is often needed to add them to the aerosol containers.

As CFC suppliers in the U.S., Western Europe, Japan, and other parts of the world develop their CFC phase-down programs, which will go beyond the Montreal Protocol, they will be focussing on rapid commercialization and application of the HCFC and HFC alternatives. The major alternative will be HFC-134a, which will replace CFC-12 in refrigeration, freezant, and air conditioning systems.

A variety of alternative aerosol packaging forms has been discussed in Part II, with a special focus on those most like regular aerosols in characteristics. All the alternatives have subsidiary positions in the marketplace, if the volume of each is compared with the 3,000,000,000-unit volume of aerosols. Several have been available for many years but have not significantly penetrated the market for several reasons, shown below:

They generally cost more (finger-pumps and sticks are exceptions).

They are limited in their product compatibility.

They depend on chemical or mechanical (often manual) action to generate pressures needed to discharge the contents.

Products must be delivered as very coarse streams, pourables, paste ribbons or (sometimes) post-foaming gels -- without having the broad range of the aerosol presentation.

Sterility is generally impossible.

Sprays can deteriorate during use.

Several are incompletely tested.

Several require capital expenditures for special filling or gassing equipment.

Sizes are limited to the 3-fl.oz. to 12-fl.oz. (119- to 355-mL) range (some are even more limited).

In general, the packaging alternatives continue to be niche-fillers, working best for a very limited range of products. Sales volumes are expected to grow to some extent, however, taking some market share away from aerosols in selected areas, but without significantly affecting the aerosol business if the present mix of political, regulatory, economic, environmental, financial, and other issues remains reasonably static.

APPENDIX A
METRIC (SI) CONVERSION FACTORS

Quantity	To Convert Form	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	oz	kg	0.0283
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psig	kPa	6.895
	psig	kPa*	((psig)+14.696)x(6.895)
Temperature:	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value:	Btu/lb	kJ/kg	2.326
Enthalpy:	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentration:	oz/gal	kg/m^3	
	quarts/gal	cm^3/m^3	25.000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
Viscosity:	centipoise (CP)	Pa-s (kg/m-s)	0.001

*Calculate as indicated