AEROSOLS

1. Introduction

Classically, aerosols are particles or droplets that range from ∼0.15 to 5 μm in size and are suspended or dispersed in a gaseous medium such as air. However, the term aerosol, as used in this discussion, identifies a large number of products which are pressure-dispensed as a liquid or semisolid stream, a mist, a fairly dry to wet spray, a powder, or even a foam. This definition of aerosol focuses on the container and the method of dispensing, rather than on the form of the product.

Aerosol products were developed in the early 1940s and were the outgrowth of the so-called "bug spray" developed during World War II. This development was credited with saving the lives of many of World War II GIs who were stationed in some of the malaria infested jungles of the world. The "bug spray" was extremely effective in controlling the spread of malaria by killing the Anopheles mosquito, which was the carrier for this disease. It did not take too long to apply the principles of the "bug spray" to the development of an entire group of consumer products that were advantageous when sprayed. These products were all similar in that they depended on the power of a liquified or compressed gas to dispense the product as a spray. This concept was then applied to products where it was desirable to dispense the product as a foam, or as a semisolid.

The aerosol container has enjoyed commercial success in a wide variety of product categories. Insecticide aerosols were introduced in the late 1940s. Additional commodities, including shave foams, hair sprays, antiperspirants, deodorants, paints, spray starch, colognes, perfumes, whipped cream, and automotive products, followed in the 1950s. Medicinal metered-dose aerosol products have also been developed for use in the treatment of asthma, migraine headaches, and angina. Food aerosols included whipped toppings and creams, cheese spreads, hors d'oeuvres, flavored syrups, and a host of similar products.

Aerosol technology may be defined as involving the development, preparation, manufacture, and testing of products that depend on the power of a liquefied or compressed gas to expel the contents from a container. This definition can be extended to include the physical, chemical, and toxicological properties of both the finished aerosol system and the propellants.

The production of aerosols has increased both in the United States and worldwide, in spite of a substantial decline during the middle to late 1970s when the use of chlorofluorocarbons (CFCs) (see FLUORINE COMPOUNDS, ORGANIC INTRODUCTION) as propellants was seriously restricted. Hydrocarbons

Table 1. **Production of Aerosols in the United States, 1985–2000, Millions of Units**

	Year						
Aerosol product category	1985	1989	1990	1995	1998	1999	2000
personal products[a]	879	1015	1050	1007	941	952	930
household products	630	680	680	725	785	802	802
automotive, industrial	342	475	415	420	433	444	446
paints, finishes	290	350	350	374	468	446	440
insect sprays	190	197	190	184	185	208	201
food products	140	175	175	252	298	323	335
animal products	15	8	8	6	2	3	3
miscellaneous	23	12	15	34	23	25	43
Total	*2509*	*2912*	*2883*	*3002*	*3135*	*3203*	*3200*

[a] Medical Aerosols are included in the personal products category and in 1999 amounted to ~14 million units and in 2000 amounted to ~28 million units.

and compressed gases (qv) have since replaced the CFCs as propellants and aerosols continue to be used by the general public. As seen in Table 1, U.S. aerosol production reached 3200 million units in 2000, which was about the same as in 1999. Although the personal products category continued to grow through 1995, a slight decrease was noted from 1996 to date, most likely due to changes in hair styles that affected the use of hair sprays and mousses.

Personal products were the fastest growing segment of the aerosol industry and still represent the largest of the categories. However, the sales of these products have declined during the past few years and a further decline may be seen in the future. Other areas of growth in this category occurred in underarm deodorants, antiperspirants, pharmaceuticals, and industrial products, which should keep this category as the largest segment of the aerosol industry.

2. Advantages of Aerosol Packaging

Aerosol products are hermetically sealed, ensuring that the contents cannot leak, spill, or be contaminated. The aerosol packages can be considered to be tamperproof. Aerosols deliver the product in an efficient manner generating little waste, often to sites of difficult access. By control of particle size, spray pattern, and volume delivered per second, the product can be applied directly without contact by the user. For example, use of aerosol pesticides can minimize user exposure and aerosol first-aid products can soothe without applying painful pressure to a wound. Spray contact lens solutions can be applied directly and aerosol lubricants (qv) can be used on machinery in operation. Some preparations, such as stable foams, can only be packaged as aerosols. Spray shaving creams and furniture polish are examples of stable foams.

The use of metered-dose valves in aerosol medical applications permits an exact dosage of an active drug to be delivered to the respiratory system where it can act locally or be systemically absorbed. For example, inhalers prescribed for asthmatics produce a fine mist that can penetrate into the bronchial tubes (see ANTIASTHMATIC AGENTS). Recent developments include the administration of insulin and other hormones by oral inhalation; thereby eliminating an injection.

3. Formulation of Aerosols

Aerosols are unique. The various components are all part of the product, and in the aerosol industry, the formulating chemist must be familiar with the entire package assembly and each of its components. All aerosols consist of product concentrate, propellant, container, and valve (including an actuator and dip tube). There are many variations of these components, and only when each component is properly selected and assembled does a suitable aerosol product result. A typical aerosol system is shown in Figure 1.

The aerosol formulater must be knowledgeable about the availability and usage of propellents, various valves and containers, including pressure limitations and construction features, as well as any other components necessary for the product concentrate system. In contrast, the formulation of a nonaerosol

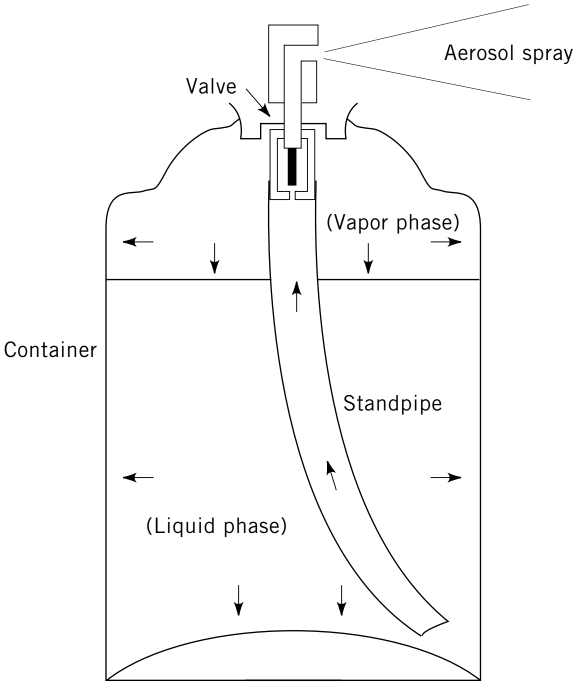

Fig. 1. Solution-type aerosol system in which internal pressure is typically (35–40 psi) at 21°C. To convert kPa to psi, multiply by 0.145.

product is not, to any great extent, affected by either the container or package closure. Nonaerosol products packaged using a pump type system may be an exception, however, as the closure can also play a role in the way a product formulation will be dispensed.

3.1. Product Concentrate.

The product concentrate for an aerosol contains the active ingredient and any solvent or filler necessary. Various propellent and valve systems, which must consider the solvency and viscosity of the concentrate–propellent blend, may be used to deliver the product from the aerosol container. Systems can be formulated as solutions, emulsions, dispersions, dry powders, and pastes.

Solutions. To deliver a spray, the formulated aerosol product should be as homogeneous as possible. That is, the active ingredients, the solvent, and the propellant should form a solution. Because the widely used hydrocarbon propellants do not always have the desired solubility characteristics for all the components in the product concentrate, special formulating techniques using solvents such as alcohols (qv), acetone (qv), and glycols (qv), are employed.

The rate of spray is determined by propellant concentration, the solvent used, valve characteristics, and vapor pressure. The pressure must be high enough to deliver the product at the desired rate under the required operating conditions. For example, a windshield ice remover that is likely to be used around 0°C must be formulated to provide an adequate pressure at that temperature. Spray dryness or wetness and droplet size depend upon propellant concentration.

Generally, aerosol packaging consists of many delicately balanced variables. Even hardware design plays an important part. For example, valves that produce considerable breakup are used for the warm sensation desired in some personal products.

Emulsions. Aerosol emulsions (qv) may be oil in water (o/w), such as shaving creams, or water in oil (w/o), such as air fresheners and polishes. These aerosols consist of active ingredients, an aqueous or nonaqueous vehicle, a surfactant, and a propellant, and can be emitted as a foam or as a spray.

Foams. Systems that dispense foams (qv) are generally o/w emulsions, although nonaqueous solvents can also be used as the external phase. When the propellant is a hydrocarbon such as an isobutane–propane blend, as little as 3–4% in a 90–97% emulsion concentrate is sufficient to produce a suitable foam. Although the majority of the propellant is emulsified, some vaporizes and is present in the head space. The resultant pressure is generally on the order of 276 kPa (40 psig). When the valve is depressed, the pressure forces the emulsion up the dip tube and out of the container. Depending on the formulation, either a stable foam, such as would be expected in a shaving cream, or a quick-breaking foam, which collapses in a relatively short period of time, appears. The propellant is an important part of the formulation and is generally considered to be part of the immiscible phase. When the propellant is included in the internal phase, a foam is emitted; when the propellent is in the external phase, the product is dispensed as a spray. Figure 2 illustrates these situations.

When the propellant is in the internal phase (Fig. 2**a**), the propellant vapor, upon discharge, must pass through the emulsion formulation in order to escape into the atmosphere. In traveling through this emulsion, the trapped propellant forms a foam matrix. These systems, are typically oil-in-water emulsions.

An emulsion system in which the propellant is in the external or continuous phase is shown in Figure 2**b**. As the liquefied propellant vaporizes, it escapes directly into the atmosphere, leaving behind droplets of the formulation that are emitted as a wet spray. This system is typical of many water-based aerosols or w/o emulsions.

Extended stability testing is a necessity for emulsion systems in metal containers because of the corrosion potential of water and some of the other ingredients. In most cases where a stable emulsion exists, there is less corrosion potential in a w/o system because the water is the internal phase.

Quick-breaking foams consist of a miscible solvent system such ethanol (qv) [64-17-5] and water, and a surfactant that is soluble in one of the solvents but not in both. These foams are advantageous for topical application of pharmaceuticals because, once the foam hits the affected area, the foam collapses, delivering the product to the wound without further injury from mechanical dispersion. This method is especially useful for treatment of burns. Some personal products such as nail polish remover, after-shave lotion, and foot and body lotions have also been formulated as quick-breaking foams.

Two advantages of foam systems over sprays (qv) are the increased control of the area to which the product is delivered and the decreased incidence of airborne particle release.

Sprays. Aerosol spray emulsions are of the water-in-oil type. The preferred propellant is a hydrocarbon or mixed hydrocarbon–hydrofluorocarbon.

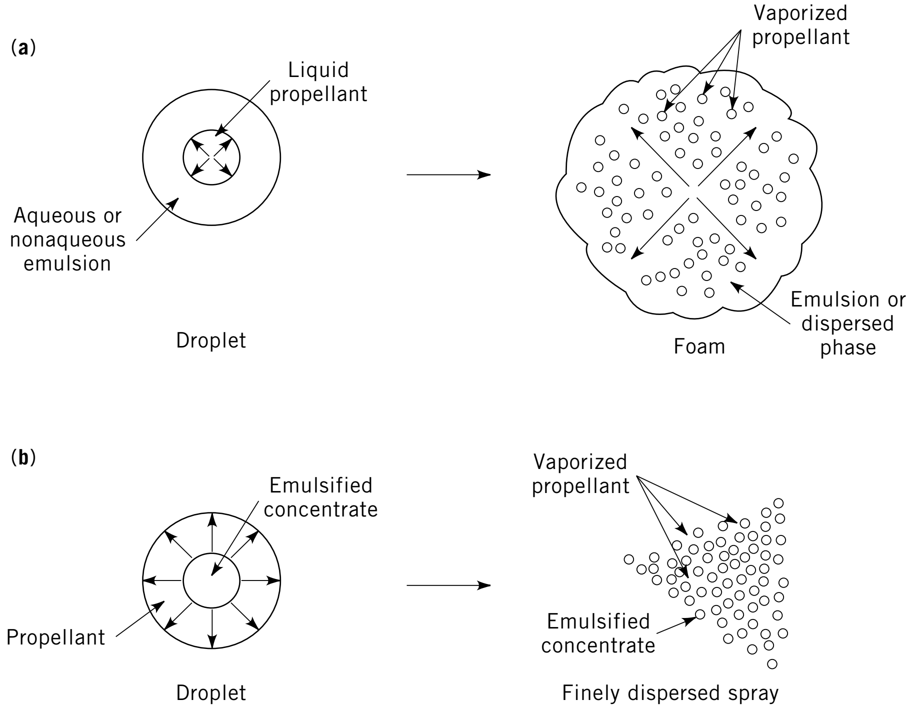

Fig. 2. Aerosol emulsion droplets containing propellant (**a**) in the internal phase with subsequent formation of aerosol foam and (**b**) in the external phase with subsequent formation of a wet spray.

About 25–30% propellent, miscible with the oil, remains in the external phase of the emulsion. When this system is dispensed, the propellant vaporizes, leaving behind droplets of the w/o emulsion (Fig. 2**b**). A vapor tap valve, which tends to produce finely dispersed particles, is employed. Because the propellant and the product concentrate tend to separate on standing, products formulated using this system, such as pesticides and room deodorants, must be shaken before use.

Dispersions. In a powder aerosol, the powder is dispersed or suspended in propellant using dispersants (qv) (oily vehicles) and suspending agents. Moisture content should be below 300 ppm and compacting, agglomeration, and sedimentation need to be minimized so that a fine powder can be uniformly dispensed without clogging of the valve. Powders must have a particle size of <40 μm (325 mesh screen) to pass through the valve orifices. Sedimentation rate can be substantially reduced by adjusting the density of either the propellant or the powder. Techniques include using a mixture of propellants of varying densities and adding an inert powder to the active ingredients. The use of surfactants (qv) as dispersing agents can also serve to lubricate the valve to prevent its sticking.

Pharmaceutical powder aerosols have more stringent requirements placed upon the formulation regarding moisture, particle size, and the valve. For metered-dose inhalers (MDIs), the dispensed product must be delivered as a spray having a relatively small (3–6 μm) particle size so that the particles can be deposited at the proper site in the respiratory system. On the other hand, topical powders must be formulated to minimize the number of particles in the 3–6-μm range because of the adverse effects on the body if these materials are accidently inhaled.

Pastes. Aerosols utilizing a paste as the product concentrate base differ from other formulations in that the product and the propellant do not come in contact with one another. The paste is placed in a bag that is attached to the valve system and fitted into the container. The propellant is then placed between the bag and the inside wall of the container so that the propellant presses against the outside of the bag, dispensing the contents through the valve.

3.2. Propellants. The propellant, said to be the heart of an aerosol system, maintains a suitable pressure within the container and expels the product once the valve is opened. Propellants may be either a liquefied halocarbon, hydrocarbon, or halocarbon–hydrocarbon blend, or a compressed gas such as carbon dioxide (qv), nitrogen (qv), or nitrous oxide.

Liquefied Gas Propellants. One of the advantages in using a liquefied gas propellant is that the pressure in the aerosol container remains constant until the contents are completely expelled. The disadvantages are that the hydrocarbons are flammable.

Chlorofluorocarbons. Prior to 1978 most aerosol products contained CFC propellants. Since that time, the use of chlorinated fluorocarbons for aerosols has been seriously curtailed. These compounds have been implicated in the depeletion of the ozone (qv) layer and are considered to be greenhouse gases (see AIR POLLUTION; ATMOSPHERIC MODELING). Starting in 1978–1979 most household aerosols were reformulated using an environmentally acceptable propellant such as a hydrocarbon.

The 1990 Clean Air Act regulates the production and use of CFCs, hydrochlorocarbons, hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbon (HFC) substitutes. CFC and halon (Class I substances) usage was phased out in steps until total phaseout occured on January 1, 1997.

In the United States, use of CFC propellants, designated as Propellants 11, 12, and 114, is strictly limited, to specialized medicinal aerosol products such as MDIs. for asthma. Most of the countries of the world (except Third World countries) have also banned the use of CFC's for all aerosols except pharmaceutical and medicinal use. The U.S. Food and Drug Administration (FDA) does not intend to prohibit the use of these CFCs in the exempted MDIs until such time as a sufficient number of alternative inhalers become available and their use has been accepted by both patient and physician.

The physical properties and chemical names of these propellents are given in Table 2.

Fluorocarbons are assigned numbers based on their chemical composition and, in general, these numbers are preceded by a manufacturer's trademark. In the numbering system, the digit on the right denotes the number of fluorine atoms in the compound; the second digit from the right indicates the number of hydrogen atoms plus 1; and the third digit from the right indicates the number of carbon atoms less 1. In the case of isomers, each has the same number. The most symmetrical is indicated by the number without any letter following it. As the

Table 2. **Physical Properties of Chlorofluorocarbon and Hydrocarbon Propellants**

	Propellant					
Property	11	12	114	A-108	A-31	A-17
chemical name	trichloromonofluoromethane	dichlorodifluoromethane	1,2-dichloro-1,1,2,2-tetrafluoroethane	propane	isobutane	*n*-butane
CAS Registry Number	[75-69-4]	[75-71-8]	[76-14-2]	[74-98-6]	[75-28-5]	[106-97-8]
formula	CCl_3F	CCl_2F_2	$CClF_2CClF_2$	C_3H_8	$HC(CH_3)_3$	C_4H_{10}
molecular weight	137.4	120.9	170.9	44.1	58.1	58.1
boiling point, °C	23.8	−29.8	3.6	−42.2	−10.2	−0.6
vapor pressure, kPa[a]						
21°C	194	585	190	846	315	214
54°C	269	1349	507	1893	763	556
liquid density, g/mL, 21°C	1.485	1.325	1.468	0.5005[b]	0.5788[b]	0.5571[b]
flammability limit, vol % in air	nonflammable	nonflammable	nonflammable	2.3–7.3	1.8–8.4	1.6–6.5

[a] To convert kPa to psi, multiply by 0.145.

[b] At 68°C.

isomers become more unsymmetrical, the letters a, b, and c are appended. If a molecule is cyclic, the number is preceded by C.

Hydrocarbons. Hydrocarbons such as propane, butane, and isobutane, butane, and isobutane, have been the replacement for CFCs in most household and industrial aerosols. They are assigned numbers based upon their vapor pressure in psia at 21°C. For example, as shown in Table 2, aerosol-grade propane is known as A-108, *n*-butane as A-17. Blends of hydrocarbons, eg, A-46, and blends of hydrocarbons and hydrochlorocarbons or HCFCs are also used. The chief drawback to the use of hydrocarbon propellants is their flammability.

Hydrocarbons have, for the most part, replaced CFCs as propellants. Most personal products such as hair sprays, deodorants, and antiperspirants, as well as household aerosols, are formulated using hydrocarbons or some form of hydrocarbon–halocarbon blend. Blends provide customized vapor pressures and, if halocarbons are utilized, a decrease in flammability. Some blends form azeotropes that have a constant vapor pressure and do not fractionate as the contents of the container are used.

As with fluorocarbons, a range of pressures can be obtained by mixing various hydrocarbons in varying proportions. As the composition of the hydrocarbons is likely to vary somewhat, depending on their source, blending of hydrocarbons must be based on the final pressure desired and not on the basis of a stated proportion of each component, the pressure of which will depend on its purity. Table 3 lists some commonly used blends that are commercially available.

Hydrofluorocarbons and Hydrochlorofluorocarbons. The properties of HFC and HCFC propellants are given in Table 4. Propellant 22 is nonflammable and can be mixed to form nonflammable blends. Some of these propellants are scheduled for phase-out by 2015–2030. Propellants 142b and 152a, especially the latter is used as the propellant of choice for hair mousse which is available as a foam.

Compressed Gas Propellants. The compressed gas propellants, so named because they are gaseous in conventional aerosol containers, are nontoxic, nonflammable, low in cost, and very inert. When used in aerosols, however, the pressure in the container drops as the contents are depleted. Although the problem is lessened when the contents are materials in which the propellant is

Table 3. **Commonly Used Hydrocarbon Blends**

		Composition (mol%)		
Designation	Pressure, psig at 70°F (21.1°C)	*n*-Butane	Propane	Isobutane
A-108	108 ± 4	traces	99	1
A-31	31 ± 2	3	1	96
A-17	17 ± 2	98	traces	2
A-24	24 ± 2	49.2	0.6	50
A-40	40 ± 2	2	12	86
A-46	46 ± 2	2	20	78
A-52	52 ± 2	2	28	70
A-70	70 ± 2	1	51	48

Table 4. **Properties of Hydrofluorocarbon and Hydrochlorofluorocarbon Propellants**

	Propellant		
Property	22	142b	152a
chemical name	chlorodifluoromethane	1-chloro-1,1-difluoroethane	1,1-difluoroethane
CAS Registry Number	[75-68-6]	[75-68-3]	[75-37-6]
formula	$CHClF_2$	$C_2H_3ClF_2$	$C_2H_4F_2$
molecular weight	86.5	100.5	66.1
boiling point, °C	−40.8	−9.44	−23.0
vapor pressure, kPa[a]			
21°C	834	200	434
54°C	2048	669	1220
density, g/mL at 21°C	1.21	1.12	0.91
solubility in water, wt % at 21°C	3.0	0.5	1.7
Kauri-butanol value	25	20	11
flammability limit, vol % in air	nonflammable	6.3–14.8	3.9–16.9
flash point, °C	none	none	<−50°

[a] To convert kPa to psi, multiply by 0.145.

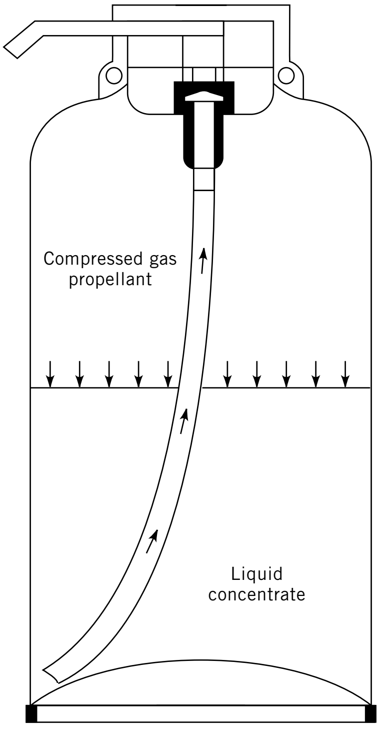

Fig. 3. Compressed gas aerosol using an insoluble gas as propellant.

Table 5. **Properties of the Compressed Gas Propellants**

Property	Carbon dioxide	Nitrous oxide	Nitrogen
CAS Registry Number	[124-38-9]	[10024-97-2]	[7727-37-9]
formula	CO_2	N_2O	N_2
molecular weight	44.0	44.0	28.0
boiling point, °C	−78	−88	−196
critical temperature, °C	31	37	−111
vapor pressure, kPa[a] at 21°C	5772	4966	
solubility in water, vol gas/vol liq at 21°C and 101.3 kPa[a]	0.82	0.6	0.016
flammability limits, vol % in air	nonflammable	nonflammable	nonflammable
flash point, °C	none	none	none

[a] To convert kPa to psi, multiply by 0.145.

somewhat soluble, this pressure drop may cause changes in the rate and characteristics of the aerosol spray. A compressed gas aerosol system is illustrated in Figure 3.

Considerable developmental effort is being devoted to aerosol formulations using the compressed gases given in Table 5. These propellants are used in some food and industrial aerosols. Carbon dioxide and nitrous oxide, which tend to be more soluble, are often preferred. When some of the compressed gas dissolves in the product concentrate, there is partial replenishment of the headspace as the gas is expelled. Hence, the greater the gas solubility, the more gas is available to maintain the initial conditions.

Compressed gas systems were originally developed simply to provide a means of expelling a product from its container when the valve was depressed. Semisolid products such as a cream, ointment, or caulking compound are dispensed as such. A liquid concentrate and a compressed gas propellant (Fig. 3) produce a spray when a mechanical breakup actuator is used. Nitrogen, insoluble in most materials, is generally used as the propellant.

Aerosols using an insoluble gas are not intended to be shaken before use. Shaking causes some of the propellant to be dispersed in the liquid concentrate. Although the product may then be dispersed to a greater extent, greater loss of propellant also results. If enough propellant is lost, the product will become inoperative.

When gases that are somewhat soluble in a liquid concentrate are used, both concentrate and dissolved gas are expelled. The dissolved gas then tends to escape into the atmosphere, dispersing the liquid into fine particles. The pressure within the container decreases as the product is dispersed because the volume occupied by the gas increases. Some of the gas then comes out of solution, partially restoring the original pressure. This type of soluble compressed gas system has been used for whipped creams and toppings and is ideal for use with antistick cooking oil sprays. It is also used for household and cosmetic products either where hydrocarbon propellants cannot be used or where hydrocarbons are undesirable.

Other Propellants. Dimethyl ether (DME) [115-10-6] is also used as an aerosol propellant. DME is soluble in water, as shown in Table 6. Although

Table 6. **Properties of DME Propellant**

Property	Value
CAS Registry Number	[115-10-6]
formula	CH_3OCH_3
molecular weight	46.07
boiling point, °C	−24.8
vapor pressure, kPa[a]	
21°C	434
54°C	1200
density, g/mL at 21°C	0.66
solubility in water, wt % at 21°C and autogenous pressure	34
Kauri-butanol value	60
flammability limits in air, vol %	3.4−1.8
flash point, °C	−41

[a] To convert kPa to psi, multiply by 0.145.

this solubility reduces DMEs vapor pressure in aqueous systems, the total aerosol solvent content may be lowered by using DME as a propellant. The chief disadvantage is that DME is flammable and must be handled with caution.

Alternative Liquified Gas Propellants (HCFCs and HFCs). Many aerosols were developed originally using CFCs 11, 12, and 114. These propellants have found widespread use due to their inertness, nonflammability, and nontoxicity. Unfortunately, the CFCs have been implicated in depleting the ozone layer, and their use as an aerosol propellant has practically been eliminated.

Topical pharmaceutical aerosols have been successfully reformulated with Propellants 152a, 142b, 22, DME, hydrocarbons, and compressed gases. Suitable valves are available which, together with modifications in formulation and propellant blends, produce topical aerosol pharmaceuticals, that are satisfactory and acceptable.

Several new liquified gas materials have been developed to replace the CFCs as refrigerants, foaming agents and in other nonpharmaceutical uses. Propellants 134a and 227 were developed as a substitute for Propellant 12 in MDIs and have survived many of the short- and long term toxicity studies. To date, no suitable replacement has been found for Propellants 11 and 114. Propellant 114 is not essential for use with MDIs, but most of the present suspension formulations require a minimum amount of Propellant 11. Propellant 11 is used to form a slurry with the active ingredient and dispersing agent, which is impossible to accomplish with Propellants 134a and R-227 (unless these propellants are chilled well below their boiling point and handled as a cold fill). The hydrochlorocarbons (HFCs) are extremely poor solvents and will not dissolve a sufficient amount of the currently used FDA approved surfactants (oleic acid, sorbitan trioleate, and soya lecithin).

It also has been noted that many of the currently used dispersing agents are not compatible with these newer materials used in valves. The gaskets and sealing compounds used in metered-dose valves present compatibility problems to the formulator; however, other gaskets have been developed and were found to be satisfactory. Several of the critical properties of these newer propellants are shown in Table 7.

Table 7. **Properties of HFCs**

Property	Tetrafluoroethane	Heptafluoropropane
molecular formula	CF_3CH_2F	CF_3CHFCF_3
numerical designation	134a	227
molecular weight	102	170
boiling point (1 atm)		
°F	−15.0	−3.2
°C	−26.2	−16.5
vapor pressure (psig)		
70°F	71.1	43 (at 20°C)
130°F	198.7	—
liquid density (g/mL) (21.1°C)	1.22	1.41
flammability	nonflammable	nonflammable
solubility in water (% w/w)	0.150	0.058

4. Components

4.1. Containers. Aerosol containers, made to withstand a certain amount of pressure, vary in both size and materials of construction. They are manufactured from tin-plated steel, aluminum, and glass. The most popular aerosol container is the three-piece tin-plated steel container. Glass containers, which are usually plastic coated, generally have thicker walls than conventional glass bottles. They are limited to a maximum size of ~120 mL and are generally used for pharmaceutical and cosmetic aerosols.

Steel. The steel container's most usual form is cylindrical with a concave (or flat) bottom and a convex top dome with a circular opening finished to receive a valve with a standard 2.54-cm (1″) opening. The three pieces (body, bottom, and top) are produced separately and joined together by high speed manufacturing. The size of the container is described by its diameter and height to top seam, in that order. Hence, a 202 × 509 container is 54.0 mm ($2\,\frac{2}{16}$ in.) in diameter by 141.3 mm ($5\,\frac{9}{16}$ in.) high. Tables of available sizes and overflow volumes and suggested fill levels can be readily obtained from container manufacturers.

Tin-plated steel was long the mainstay of the U.S. aerosol industry and still represents a very large volume. The tin coating provides both protective internal and external surfaces and the means for soldering the flat body plate into a leak-proof cylinder. Both tin and lead solders have been used in the past but at present has been largely replaced by welded side-seam construction.

The welding process has a slight financial advantage because it eliminates the need for tin. In addition, the welded joint is esthetically more desirable, it is less than one-half the width of the soldered joint, and it does not weaken during prolonged storage at elevated temperatures.

In order to increase resistance of the container to the effect of the product or to protect the product from the tin plating, an inert, internal organic coating can be applied.

Aluminum. The majority of aluminum containers are of monobloc (one-piece) construction, impact extruded from a slug of lubricated aluminum alloy. These containers are widely used for many products and are available in a vast array of heights and diameters. Because these containers lend themselves to additional shaping, many unusual shapes can be found in the marketplace. They may also be coated after the extrusion process.

Aluminum containers are recommended for many applications because of the very hard, corrosion-resistant oxide coating. They are deficient in only one respect: Once the protective skin has been penetrated, aluminum corrosion accelerates.

Two-piece aluminum containers are also available. These consist of impact-extruded upper shells having a seamed-on aluminum bottom. The valve opening is machined from the solid aluminum rather than rolled. All coatings must be applied to the can body after the forming operation.

Glass. Glass containers present completely different design considerations from metal ones. They are totally nonreactive with the product, free of potentially leaking seams (the valve joint may be an exception), transparent or opaque as desired, and can be beautiful in design. The larger sizes attract attention on store shelves. On the other hand, they can break in manufacture, in shipping, and in usage. Although the extent and hazards of breakage can be reduced by means of a thick vinyl coating, glass containers are heavy, making them most costly to ship. Glass containers are processed more slowly and have higher scrap rates, and are generally limited to low pressure product systems.

4.2. Valves. The dispensing valve and actuator serve to close the opening through which the product and frequently the propellant entered the container, to retain the pressure within the container and to dispense the product in the precise form and dosage intended by the manufacturer and expected by the consumer. An aerosol valve, shown in Figure 4, consists of seven components. Many variations exist both for special purposes and to avoid existing patents.

The *mounting cup* (ferrule for bottle valves) mechanically joins the valve to the container. The mounting cup may be made from a variety of materials, but is typically tin-plated steel or aluminum coated on the underside. It contains the gasket that provides the seal. Soft gasketing material is applied wet and bonded in place or, more frequently in larger cans, cut rubber, polyethylene, or polypropylene gaskets are used.

The *housing* physically holds the valve pieces together by means of a mechanical lock (crimp) and fits into the pedestal of the mounting cup. It is made from any of a number of common thermoplastics and contains the metering orifices for both the liquid and vapor phases of the effluent. Many valves do not meter vapor; the flow of the liquid is controlled by other means. A vapor tap may also be present to reduce the flammability of the product when it is emitted or to produce a finer, drier spray.

The plastic *stem* is the movable segment of the valve. It provides the opening mechanism and usually contains another metering orifice as shown.

The *spring* ensures a solid closing action and is usually wound from stainless steel wire. The *dip tube* conducts the product from the container to the valve. It is usually extruded from polyethylene or polypropylene and has an inside diameter of >2.54 mm, although it can be provided in capillary sizes having diameters down to 0.25 mm. These small tubes are used to reduce flow rate and may function in place of the liquid metering orifice in the valve housing.

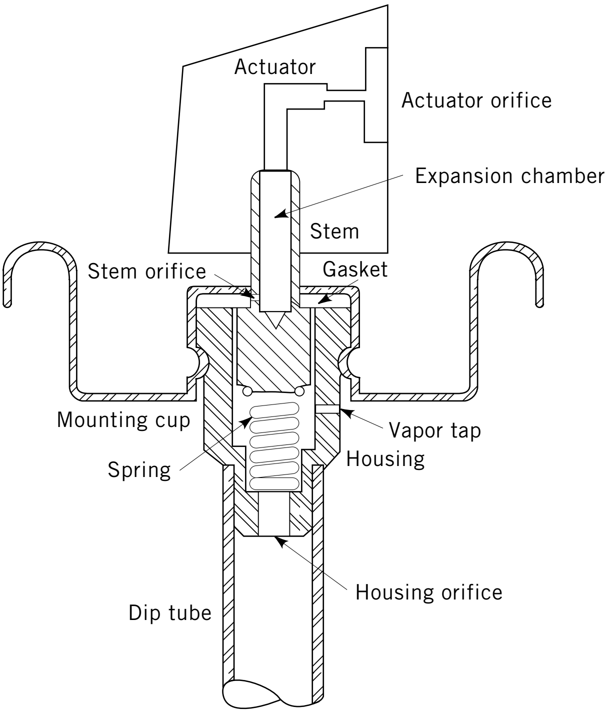

Fig. 4. Aerosol valve components.

The *actuator* contains the final orifice and a finger pad or mechanical linkage for on–off control. The spray pattern is largely affected by the construction of the actuator, particularly by the chamber preceding the orifice. Actuators are often termed mechanical breakup and nonmechanical breakup depending on the complexity of this chamber. Mechanical breakup actuators are of more expensive two-piece construction. Actuators are usually molded from polyethylene or polypropylene; the breakup insert may be almost any material, including metal.

Valves may differ depending on the form of the product. Manufacturers stock a wide array of standard components. In addition, most are willing to produce unique combinations at no additional charge if no major tooling changes are required. The largest numbers of aerosol valves are used to produce sprays. These are actuated by either tilting forward or depressing vertically. Foam valves differ from spray valves primarily in the actuator, which is relatively wide open. Small actuator orifices throw the foam and are used for products such as rug shampoos and decorative snow. Internally, foam valves have no vapor tap and contain relatively large orifices.

Metering valves are used extensively in the pharmaceutical field for inhalers and other products requiring controlled dosage delivery. They typically deliver 50 to 150 mg of product per stroke with good repeatability. The metering is achieved by plugging the body orifice with the downward stroke of the stem, allowing only the product in the housing (metering chamber) to escape.

Codispensing valve (and container) systems are used for products that consist of two reactive ingredients that must be kept separate until dispensed. They can deliver the product components in stoichiometrically correct amounts, thoroughly mixing them in the process. Successful use of these systems requires proper metering throughout the life of the container, safety considerations (should the internal seals between reactants fail), acceptably low permeation across internal membranes, end-use excess of the preferred component, and the usual product–package compatibility. The codispensing valves are the most technically demanding systems in the marketplace, but to date, have not been used commercially to any great extent.

4.3. Barrier–Type Systems.

These systems separate the propellant from the product itself. The pressure on the outside of the barrier serves to push the contents from the container. The following types are available.

Piston Type. Since it is difficult to empty the contents of a semisolid from an aerosol container completely, a piston-type aerosol system has been developed. This systems utilizes a polyethylene piston fitted into an aluminum container. The concentrate is placed into the upper portion of the container. The pressure from nitrogen 621–690 kPa (~90–100 psig), or a liquified gas, pushes against the other side of the piston and, when the valve is opened, the product is dispensed. The piston scrapes against the sides of the container and dispenses most of the product concentrate. The piston-type aerosol system is shown in Figure 5. This sytem has been used successfully to package cheese spreads, cake decorating icings, and ointments. Since the products that use this system are semisolid and viscous, they are dispensed as a lazy stream rather than as a foam or spray. This system is limited to viscous materials since limpid liquids, such as water or alcohol, will pass between the wall of the container and the piston.

Piston Bag Type. This system consists of a collapsible plastic bag fitted into a standard, three-piece, tin plate container. The product is placed within the bag and the propellant is added through the bottom of the container. Since the product is placed into a plastic bag, there is no contact between the product and the container wall except for any product that may escape by permeation through the plastic bag.

Limpid liquids, such as water, can be dispensed either as a stream or fine mist depending on the type of valve used, while semisolid substances are dispensed as a stream. In order to prevent the gas from pinching the bag and preventing the dispensing of product, the inner plastic bag is accordion pleated. This system can be used for a variety of different pharmaceutical and nonpharmaceutical systems, including topical pharmaceutical products as a cream, ointment or gel.

A modification of this system dispenses the product as a gel that will then foam. By dissolving a low boiling liquid such as isopentane or pentane in the product, a foam will result when the product is placed on the hands and the warmth of the hands will cause vaporization of the solvent. This system, as well as the piston system, is used in postfoaming shave gels.

Other variations of these systems include using a laminated pouch that has been sealed onto a 1 in. valve. This unit is placed into an aluminum can, sealed and pressurized to 103–138 kPa (~15–20 psig). The product is injected into the

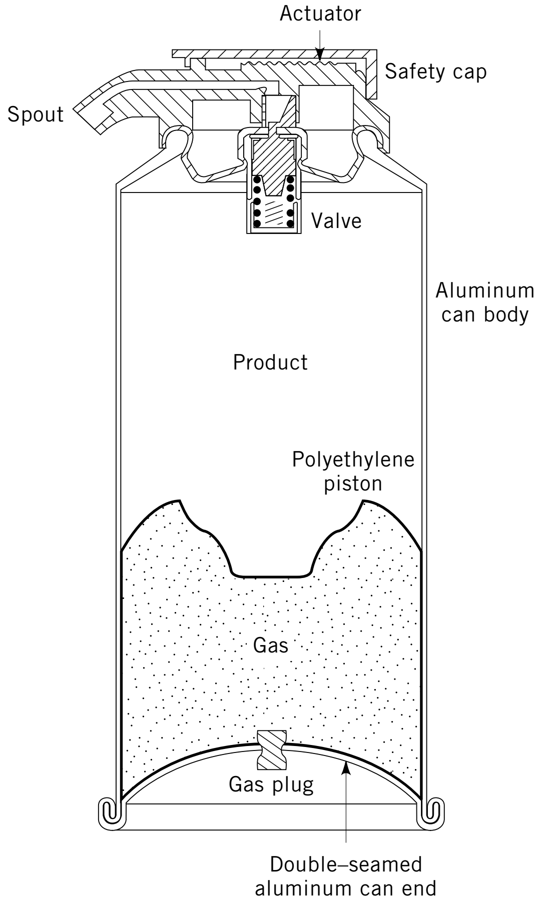

Fig. 5. Piston-type barrier pack system.

pouch, and develops a pressure of 276–345 kPa (∼40–50 psig) as the inner bag expands. Another system includes filling the product into a latex bag that then expands. The energy caused by the stressed bag will release the product when the valve is opened. These systems have been used to dispense a variety of personal care products including some pharmaceutical gel products.

5. Filling of Aerosols

All aerosols are produced by either a cold or pressure-filling process. The cold fill process has been used for some aerosols that contain a metered-dose valve, although pressure filling is now the preferred method. Generally, a concentrate is prepared which is filled into the aerosol container and then the valve is added. For the most part, pressure filling is carried out either by an under-the-cup filler or through the valve. If an under-the-cup filler is used, a vacuum is drawn, the propellant is added (under the valve cup), and then the valve is sealed in place.

Where filling is done through the valve stem, the product is first filled into the container, a valve is crimped into place, and, at the same time, a vacuum is drawn in the can. The propellant filler then forms a seal around the head of the can and under high pressure the propellant is forced through the actuator and valve stem into the container. The contents are then checked for leaks and an overcap is added to complete the process.

Nitrogen, carbon dioxide, and nitrous oxide, which are only slightly soluble in the product concentrate are packaged by placing the product into the container and then sealing a valve in place. The compressed gas is added through the valve using a gasser-/shaker-type filler.

The piston-type barrier system is filled by adding the product to the containers. The valve is then sealed into place. The propellant is added through a small hole in the bottom of the can, and the opening is sealed using a rubber plug. The propellant can be either nitrogen at 621 kPa (∼90 psig) or with ∼5–10 g of a liquid gas propellant. Valves with relatively large openings, such as foam valves, are frequently used.

The plastic bag type system consists of a collapsible plastic bag fitted into a standard three-piece, tin-plated container such as a 202 × 214, 202 × 406, or 202 × 509 can. The product is placed within the bag, the valve is sealed, and the propellant is added through the bottom of the container, which is fitted with a one-way valve. There is no limitation on the viscosity of the product but compatibility with the plastic bag must be considered. A free-flowing liquid can be dispensed either as a stream or a fine spray, depending on the type of valve employed. A viscous material is often dispensed as a stream. This system has been used for caulking compounds, postfoaming gels, and depilatories.

6. Economic Aspects

According to the Clean Air Act of 1990, as well as regulations of the FDA and the EPA, the use of CFCs in nonessential, nonexempted products has been prohibited since 1996, which included all commercial aerosol products except for a few medical aerosols (inhalers used for asthma) as well as refrigerators, freezers, and chillers. Today most of these aerosols contain a logo and the words, “Contains NO CFCs which Deplete the Ozone Layer”. (See Fig. 6).

Fig. 6. No CFC Logo.

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