

AEROSOL VALVES

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AN ESSENTIAL ELEMENT in every aerosol dispenser is the valve, which, when actuated, releases the product from confinement and allows it to go to work. Valves can be varied within surprisingly wide limits. They can deliver a very fine mist, a coarse spray, a very long stream, a foam, or even a viscous gel or paste. While most of them deliver the product at the convenient rate of about 1.0 g/s under ambient conditions, there are some that deliver as little as 0.2 g/s and others that run up to as fast as 80 g/s.

In 1970 there were at least 15 valve producers active in the U.S.A. and an estimated 40 to 60 additional valve makers in the rest of the world. These numbers have now shrunk considerably. In the U.S.A. the following firms produce virtually all the aerosol valve requirements:

Precision Valve Corporation
 Seaquist Valve Company
 Summit Packaging Systems Inc.
 ARC Division of Ethyl Corporation
 Dispensing Systems Division of Risdon Corporation
 Newman-Green, Inc.
 Emson Research, Inc.
 Clayton Corporation
 Sprayon Products, Inc.
 Avoset Corporation

Leading foreign manufacturers include many firms owned, licensed or otherwise affiliated with various U.S.A. valve makers. A partial listing of larger operations would include:

Metal Box Limited (Affiliated with Precision Valve Corporation)
 Valois, S.A. (French affiliate of Seaquist Valve Company)
 Aerosol Research Ltd. (English affiliate of Cope-Allman, Ltd.)

Reboul Sofra, S.A. (French affiliate of Cope-Allman, Ltd.)
 Coster Technologie Speciali (Italy)
 Solfrene S.p.A. (Italy)
 Deutsche Prazisions Ventil GmbH. (West Germany affiliate of Precision Valve Corporation)
 Newman-Green (U.K.) Ltd. (Wales, U.K.)
 Aervalv, S.A. (Mexico)
 Maruka Machinery Co., Ltd. (Japanese affiliate of Newman-Green, Inc.)

The Vertical Action Aerosol Valve

By far the most popular type is the vertical-acting, piston-type or push-down valve; usually just called the vertical valve. Probably 90% of all aerosol valves are made in this basic design. The operating principle is very simple. The valve opens when the stem is depressed into the body and shuts off when it is released and springs back into place. When in the normal or closed position the stem is pressed upward by a metal spring. But when a sufficient downward pressure is applied the spring tension is overcome and the stem is forced downward. This serves to slide one or more horizontal stem orifices past the seat gasket and into the top of the valve chamber, which is under pressure from the product. The pressure then forces the product through the stem orifice(s) into the vertical center hole of the stem and out through the valve button or spout.

A typical vertical-action valve has seven basic parts: the actuator, mounting cup, stem, stem gasket, spring, valve body and dip tube. Only three move in relation to the other parts: the stem, stem gasket and spring.

Actuator

The actuator may be a simple spray button, or it may be an integral part of various spouts or spray domes. As a rule, it not only allows the user to operate the valve, but it may also fulfill a major role in determining spray rate, spray pattern, particle size distribution and so forth. A very large array of actuators is available for dispensing sprays, foams and other product varieties.

The actuators are almost always injection molded from polyethylene or polypropylene, using plasticizers and other components that virtually eliminate any chance of cracking from stem tension. A number of design features are used. One, of course, is the size of the terminal orifice—where the product emerges from the dispenser. For sprayheads, the normal range is 0.013" to 0.030" (0.33 to 0.76 mm). The diameter is

generally selected in a size that is slightly larger than that of the metering orifice in the valve stem to develop a spray of better and more uniform particle size distribution.

The terminal orifice may be straight or tapered, and if tapered it may be either a forward or reverse type. In addition to the standard straight or tubular orifice, modified straight orifices are made by stepping the bore outward at a shouldering point, so that the end of the bore is larger than the beginning. Many of the "flat face" and powder spray buttons have bores that are widened near the end. If the widening takes place near the mid-point, and especially if the shoulder area is angled instead of square, the actuator will take on the properties of a "regular" or outward tapered type. Some actuators have a tubular orifice designed to accommodate a 0.090" (2.3 mm) plastic extension tube of various lengths. A tapered orifice will give a slightly better break-up than a tubular one, and the reverse tapered type will generally provide a slightly better break-up and somewhat wider pattern than either the standard or regular tapered profiles.

Actuators may be specially formed and equipped with plastic inserts to aid in the development of particularly desirable spray patterns. In general, they are called M.B.U. or mechanical break-up systems. A few are designed to produce jets and other unique patterns, but most M.B.U. actuators are used to either provide a spray with otherwise non-sprayable compositions, or to enhance the break-up provided by the propellant by adding a mechanical factor. In the case of starches or window cleaners, for instance, the products are about 90% water and they could not be marketed in aerosol form were it not for the ability of the M.B.U. actuator to break up the solid stream of liquid into an acceptable coarse spray.

The insert component is forced into the enlarged orifice area of the actuator, where it often fits over a post that is channeled on the flat end. The product enters a peripheral channel, and then goes into at least two and nearly always four offset radial channels that end at the insert orifice. The configuration acts to give the product a strong swirling action as it leaves the actuator. Taken by itself, this would result in a hollow cone type spray, able to produce a doughnut pattern on a surface. But if the offset radials are arranged correctly and if a mixing or interaction area is provided, just below the terminal insert orifice, then product from the violent mixing area will tend to fill in the hollow area, and the doughnut

type spray will change to a disc-like or normal spray. The technology of the turbulent fluid flow patterns in M.B.U. valves is still not understood completely and patterns are developed largely by empirical means. Dimensions are critically important in the channel area, as might be imagined.

By selecting the correct M.B.U. button from the scores of available types, the formulator can produce a great diversity of spray patterns and probably, among them, some that are acceptable for his product. On the negative side, M.B.U. actuators are understandably higher priced than one-piece sprayheads, and they are also somewhat more susceptible to plugging problems.

Not all M.B.U. actuators are two-piece assemblies. For example, the Precision Valve Corporation has been able to mold some acceptable one-piece types. More exacting control is generally afforded by the two-piece varieties. And finally, there are a few lines of what can be called quasi-M.B.U. actuators: one-piece sprayheads which provide more break-up than ordinary one-piece styles, yet less than the true M.B.U. systems.

Mounting Cup and Cup Gasket

The one-inch (25.4 mm) mounting cup, first developed and patented by the Bridgeport Brass Company in 1952, was one of the important early developments that helped make the aerosol package commercially practical. The cup serves to clamp the valve stem, stem gasket, spring and body together and at the same time provides an hermetic seal to the one-inch (25.4 mm) opening of the can. It also serves as both a platform and attachment area for most foam spouts, some actuator skirts and several types of overcaps and spray domes.

About 90% of all U.S.A. aerosols use valves with tinplate mounting cups. The remainder carry various ferrule type valves and one-inch mounting cups made of aluminum. Aluminum aerosol cans may carry either ferrule valves, aluminum one-inch cups or tinplate one-inch cups, depending upon size and formulation compatibility aspects.

Tinplate mounting cups are usually made of 100# baseweight steel plate, so that the average thickness is thus 0.0110" (0.280 mm). Alternate 95# and 107# baseweights are also available on special order but are rarely encountered. The regular 100# tinplate will begin to deform upward at internal can pressures of somewhat over 320 psig (2.07 MPa), and will start to leak product through the crimped seal at about 375 psig

(2.59 MPa). Since these figures exceed the deformation and burst resistance of virtually all tinplate cans and many aluminum cans, there is rarely a need to use heavier plate. Exceptions have been encountered for some cups with threaded ($\frac{7}{16}$ "-20NF) hubs, for packaged refrigerants, and for heavy-duty aluminum cans and valves, designed to meet unrealistic Underwriters Laboratories pressure criteria for a few specific products such as fire extinguishers.

Tinplate cups are available with various plating thicknesses. An 0.33# ETP specification is popular for cups that are epoxy lined. Most plain cups use 0.75# ETP. The use of tin-free steel (TFS) is being researched for eponed or Organosol/epon cups as a minor cost-saving measure. Such cups have a gray appearance. Because of this detraction they may find their initial use in applications where the valve cup is covered with a foam spout or spray dome.

Aluminum mounting cups are about 0.016" (0.4 mm) thick, or about 1½ times as thick as tinplate cups because the metal is less resistant to deformation. They can be identified by their softer, hazier or less shiny surface appearance or by the fact that they are non-magnetic. They are used only on aluminum cans these days, although in the past there have been some exceptions. Crimper settings must be revised to accommodate the greater thickness of aluminum valve cups. Aluminum cups are almost always epon protected on tops and bottoms.

Where the product is unusually active, a stainless steel mounting cup may be used, but the price increase is very significant. The typical thickness of 0.0105" (0.267 mm). Most valve companies do not stock these special cups. They must be special-ordered, and there may be delays because of this. Some years ago special

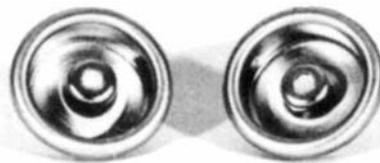


Figure 1. Flat and Conical Valve Mounting Cups

The conical variety, on the left, is used to prevent cup impingement of wide-angled sprays for other special purposes. In the illustration the valve components are not yet assembled and staked in place.

laminated cups were made by at least two firms, the steel core being overlaid with thin films of Monel, stainless steel, aluminum or other metals. A typical metal "sandwich" consisted of 0.002" Monel/0.008" steel/0.001" Monel, with the heavier 0.002" (0.05 mm) Monel layer facing the product. Plate of this type is still available but is of no current interest to the aerosol industry.

A number of specific shapes have been used for mounting cup designs. The so-called "flat cup" and "conical cup" designs are illustrated in Figure 2.

The conical profiles are often used where the actuator must be elevated somewhat in order to allow a wide-angled spray to clear the edge of the mounting cup without impingement and dripping.

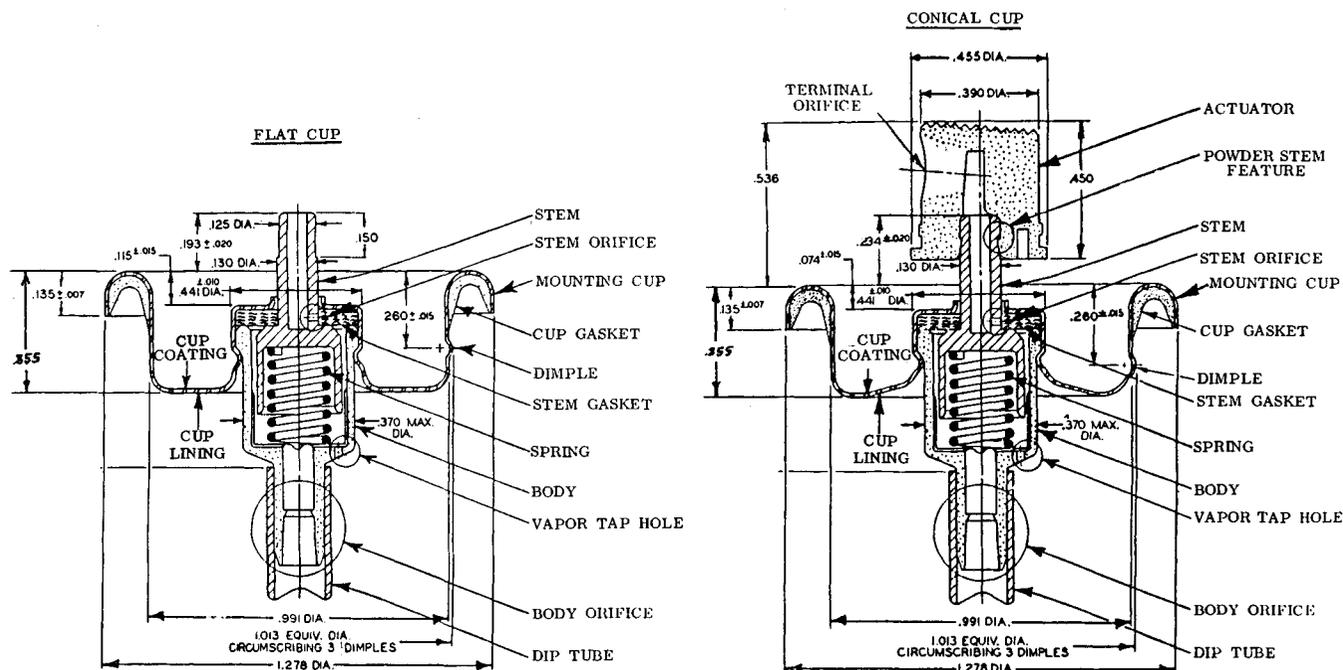
The portion of the valve cup that holds the valve assembly is called the pedestal. The cup pedestal is clamped securely over the valve body wall by means of a stake or clinch. The dimensions of this indentation must be controlled closely. If they are too loose, the valve may leak or show excessive seepage. If they are too tight or high, the stem gasket may be over-compressed, causing it to squeeze inward, toward the stem and make the valve hard to operate or to spray

poorly. Most valves have different size bodies, and thus the pedestals have a variety of diameters. This becomes important for Through-the-Valve (T-t-V) gassing operations where the adapter makes a seal around the top wall of the pedestal. Many adapters will not handle more than one, two or three valves because of this variation.

The diameter of the one-inch (25.4 mm) hole in the can dome is specified as 1.000 ± 0.004 " (25.40 ± 0.10 mm). In order to fit smoothly into the minimum diameter can plug, the diameter of the outer valve cup wall is specified as 0.991 ± 0.003 " (25.17 ± 0.07 mm). This leaves a ring of at least 0.001" (0.025 mm) to accommodate out-of-round conditions, the bottom feather-edge of Flowed-In® cup gasket materials and so forth. In some instances, valve cups are produced with smaller outside wall diameters. For example the Precision Valve Corporation's nylon-liner cup has an o.d. of about 0.956" (24.28 mm) since it is held within a lower sheath or lining of nylon about 0.20 ± 0.002 " (0.51 ± 0.05 mm) thick, to protect it from discoloration by thioglycollates contained in depilatories, for exam-

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Figure 2. Cross Section of a Typical Flat Cup and Conical Cup Valve



ple. The cup o.d. has to be made smaller to accommodate the liner and still fit within the can orifice.

In a potentially much more important example, the mounting cup used with the Precision Valve Corporation's polyethylene sleeve development must have an o.d. of 0.965 ± 0.003 " (24.51 ± 0.07 mm) to make allowance for the PE-sleeve, which runs about 0.0125 to 0.0140" (0.32 to 0.36 mm) in thickness. The PE-sleeve is designed to replace the more conventional GK-45-NV and NVH type Flowed-In[®] gaskets as well as the buna, neoprene, Viton and other cut gaskets, but it differs from them in that up to 0.014" (0.36 mm) of polyethylene is designated to hug the outer body wall. The Flowed-In[®] gaskets have only about 0.001 to 0.002" (0.025 to 0.050 mm) of thickness in this area and the cut types have none at all.

The PE-sleeve offers much promise as the future gasket of choice for the aerosol industry. It can be gassed with both T-t-V and U-t-C (pre-set) machines and has the following set of advantages:

- a. Lower cost and low anticipated future costs.
- b. No possibility of EPA actions under the Clean Air Act, as may be the case for other gasket compositions.
- c. Can be made to significantly closer dimensional tolerances than other gaskets.
- d. Shows very low clinch leakage, even with very high solvent systems.
- e. It produces a cork-like vertical seal, plus the regular seal in the arch of the cup.
- f. Gasket flaking (which may cause valve clogging) does not occur.
- g. Latent leakers are avoided.

The gasket is specially compounded from low density FDA grade polyethylene, nominally 0.014" (0.36 mm) thick. Because of the tension at the upper cut edge area when in place it has had to be formulated in such a way as to be highly resistant to environmental stress cracking. The gaskets are made in Precision Valve Corporation's Aeroclo Division plant in New Jersey, using the following six-step process:

- a. The polyethylene, in prilled form, is melted and extruded into tubes.
- b. The tubing enters a six-station machine, where it is first cut to length and placed onto the valve cup by controlling and feeding arbors.

- c. It is driven home, into the cup arch.
- d. It is conditioned for the final forming operation—tucking into the curl.
- e. The height of the sleeve and other dimensions are checked with mechanical fingers.
- f. Finished valve cups are bulk packaged for storage prior to assembly of finished valves.

Actually, dimpling (three unusually large outward dents just below the bottom edge of the sleeve) is now performed on the valve assembly line, but will later be done immediately after the checking operation (step e.). The dimples are extra large since they must protrude out past the sleeve and make a distortion fit past the can curl diameter to enter the can slightly and effectively hold the loose valve in place until the time it is crimped to the container. The equivalent diameter circumscribing the three dimples is about 1.013" (25.73 mm).

As of mid-1982 Precision had the PE-sleeve gasket available in at least four cup variables and were working on additional ones, including an aluminum cup. The cup system has patent applied status at this time. The company has offered the development to other interested valve manufacturers.

In addition to the change in cup wall diameter, other alterations are necessary to achieve final, after-crimping, stem heights. For example, the conical cup for PE-sleeve gaskets must be made deeper (0.228" going to 0.238") to get the optimum stem height of about 0.304" (7.72 mm) after crimping, so that plastic full-diameter actuating components can be seated correctly for the best operational results. The stock used for these cups is normally 0.25# ETP 100# baseweight plate. Crimping dimensions of 1.070" (27.18 mm) diameter and about 0.181 to 0.185" (4.60 to 4.70 mm) depth seem to be optimum. The cup dimples have to be about 0.020" (0.51 mm) lower than normal in order to obtain a good vacuum in the U-t-C gasser.

In 1982 (and for about thirty years previous), the GK-45 type Flowed-In[®] gasket was the standard, used in nearly all U.S.A. aerosol valve cups. The usual method of application involves pouring about a 50% dispersion of the neoprene-based material into the hollow of the inverted mounting cup, using a special nozzle, while the cup is rotating slowly. The pour period equates to 360° of rotation, although a 720° cycle has sometimes been used. After the pour, the cups are heated in three stages to drive off the solvents and chemically cure the elastomer. The thickness specifica-

tion is usually described as 0.022 ± 0.007 " (0.56 ± 0.18 mm) on an Acceptable Quality Level (AQL) of $= 0.25$, but it is very hard to maintain this specification without constant surveillance. In addition, the gasket should extend downward along the cup wall to a distance of 0.175 ± 0.015 " (4.45 ± 0.38 mm) below the crown or highest part of the mounting cup (K-dimension) with an AQL of $= 1.5$. The wet or pour weight of the gasket is generally controlled to between 475 - 500 mg per cup. The GK-45 NVH dispersion is 60% solids.

Several modifications of these dimensions and weights have been used, but always to a very insignificant extent. During the 1970s at least two valve suppliers offered cups with a so-called "double gasket". In this case the thickness was increased to $0.040 = 0.010$ " (1.02 ± 0.25 mm) (AQL $= 0.25$) with a maximum thickness variation of 0.017 " (0.43 mm) per can (AQL $= 0.25$), and the gasket height was established as 0.195 ± 0.015 " (4.95 ± 0.38 mm) at an AQL of 0.25.

Of more interest today is the "half-thick" gasket, with a wet or pour weight of 225 to 250 mg per cup. It often holds swelling-type formulations, such as methylene chloride types, more effectively than the standard gasket, and also generally costs about \$0.50/M. less.

Another variation is the "low-lined" gasket, available from Summit Packaging Systems, Inc. in both regular (445 to 475 mg) and "half-thick" varieties (225 to 250 mg - tentatively). The low-lined profile requires a change in pour nozzles and is designed to provide extra gasket compound at the vertical wall of the valve cup. It is also very effective for holding a number of products to a very low annual weight loss range.

Until about 1973 the GK-45 composition, by the Dewey & Almy Division of W.R. Grace Co., contained NA-22, a 2-mercaptoimidazoline curing agent made by E.I. du Pont de Nemours & Co. But about that time, evidence came to the FDA that the additive might be a chemical carcinogen. Although the calculated amount of unreacted imidazoline that could enter the product was only about 1×10^{-8} %, the FDA (in a housekeeping measure) asked that it be removed from both the stem and cup neoprene-type gaskets. This was done. Very high boiling, non-volatile esters were used to replace the imidazoline derivative. Depending upon the selection of additives, the GK-45 material was then revised to GK-45 NV and GK-45 NVH. The properties of these two substitute elastomers were highly comparable, so

that they were often used interchangeably. The GK-45 NVH is currently by far the most popular.

In the case of the cup gaskets only a small sacrifice of sealing properties had to be made in the transition, but the quality downgrade was somewhat more serious in the case of neoprene stem gaskets, since here a flexing action was involved also.

Several other poured-in cup gaskets have been advocated by the Dewey & Almy Division in recent years. A general problem with the GK-45 types is that they either swell or shrink excessively with some aerosol products, they require rather high and long curing oven temperatures, and they contain toluene and other solvents that are driven off during curing, to the consternation of the EPA (Clean Air Act) and OSHA (from possible worker exposure). D&A's GK-70 was of interest for a time in that it did not shrink with such compositions as ether or ethanol/P-12 personal deodorants and disinfectant/deodorants, but when P-12 was removed from the U.S.A. aerosol market the material went into a decline and is now an almost extinct special order item.

Water-based latexes have been under intense development for several years because of the environmental and possible health concerns relating to toluene cook-offs during curing of the solvent-based types. They are also less costly, and presently run about \$1.15/lb. (\$2.54/kg). D&A's Cap 5520 and W-1809 waterbase mounting cup compounds have the properties listed in Table I.

The D&A Cap 5520 latex emulsion was developed by the company's overseas division in Great Britain and has been run commercially by Metal Box Limited and other European valve makers for many years. About 1979 an effort was made to introduce this product into the U.S.A. by importation from England. A major valve cup supplier in the Chicago area attempted to pour mounting cups with it but experienced a series of production problems. Marginally acceptable cups were finally produced, but still showed a certain amount of leakage, due to fish-eyes, voids, poor cup adhesion, pin-holding, rippling and in general a non-homogeneous lay-down of the elastomer. However, cups hand selected for good quality pours gave better performance than GK-45 NVH cups, in the case of formulations high in methylene chloride.

The reason for the U.S.A. production problems have never been explained. They may relate to pot-life, to cooling of the drums during trans-Atlantic air ship-

ment, or to other factors. At any rate, the final result is that this emulsion is no longer offered in the U.S.A.

The D&A Darex W-1809 latex emulsion, made at the Dewey & Almy Woodbury, NJ facility, represented an attempt to produce a product essentially equivalent to the European Cap 5520 material. It became available commercially about 1978. Testing revealed that cup adhesion and solvent resistance were inferior to GK-45 NVH, and that some exudation occurred with CO₂ packs and other higher pressure formulas. In the case of formulas containing 20 to 70% of methylene chloride, weight losses were less than those found for GK-45 NVH. A lower shoulder placement was required, up to 0.016" (0.040 mm) above the valve skirt height, in order to prevent the compound from oozing into the container during the heavy compression stage immediately prior to U-t-C crimping.

TABLE I

Properties and Recommendations for D&A Cup Latexes

Attributes	Cap 5520	W-1809
<u>Physical Properties</u>		
Color (Liquid)	Red	Red
Color (Dried, cured solid)	Red	Red
Viscosity (cps at 77°F or 25°C)*	2900 to 4000	2300 to 2800
Total Solids (%w/w)	83.5 to 84.5	82.5 to 83.5
Specific Gravity (wet)	1.96	1.94
Specific Gravity (dried film)	2.42	2.34
Durometer (Shore A)	—	74
Diluent	Water	Water
<u>Lining Conditions</u>		
Nozzle Size	54 drill	56 drill
Air pressure (psig)	10 to 20	10 to 20
Film Weight (wet) (mg)	650 to 675	600
Film Volume (dry) (gauge) (inch)	0.028	0.025
Shoulder placement	0 to 0.016" above curl	Even with curl
Lining speeds	Slow	Slow
<u>Curing Cycle</u>		
Air Dry (max.) (minutes)	15	15
Time per Zone, and Temperature °F)		
Zone 1	30 at 135	30 at 130/135
Zone 2	30 at 155	30 at 150/155
Zone 3	30 at 195	30 at 190/195
Price (\$/lb in 80 lb pails - 1980)	85	88.5
FDA Status 1980	Applied for	Approved

*Brookfield Viscometer, Model LVF, Spindle #3 at 60 rpm.

In 1979, D&A learned that certain ingredients, including a critical emulsifier, were being discontinued in this country. In response, they abandoned plans to improve upon W-1809 and began researching new compositions that might equal GK-45 NVH's performance profile. During 1980, supplies of the discontinued ingredients became exhausted. It was not considered economically feasible to import European equivalents, so the W-1809 program was suspended.

A third water-based cup gasket material is identified as the Wiederhold latex emulsion, or (more simply) WDH Compound or CAP 85-64. It is a red, viscous liquid made in West Germany and used in many European countries. In the U.S.A. it is available from at least two valve manufacturers on special order.

Cured WDH gaskets are very sensitive to humidity and are able to absorb up to about 8% water. The material is relatively soft under any conditions, but with absorbed water it becomes even softer and more flowable under pressure. In many cases, WDH type valves, stored at 50% R.H., have shown a significant degree of ooze, or extrusion, when gassed and crimped by a U-t-C machine. The same valves, pre-heated in incubators at 160°F (71°C) to drive off the preponderance of any absorbed water, did not show any oozing. But even where enough gasket material squeezes out to give a severe draping effect the crimp seal integrity always seems to remain intact, with very low weight losses. The gasket material appears to adhere better to epon lined cups than to plain ones, but even on plain types it is better than D&A's Cap 5520. It is especially good for products high in chlorinated solvents, such as methylene chloride. There is a report that the material caused corrosion of bright, machine-finished aluminum can beads.

The future of WDH latex in the U.S.A. is uncertain at best. There are concerns about pot life, and about the possibility of freezing the emulsion if it is air-freighted across the North Atlantic during the winter months, and perhaps even during the summer. A number of domestic productions have been made successfully, but if the PE-sleeve gasket lives up to present expectations it will do everything the WDH will do, and more cheaply as well.

A number of firms apply poured-in gasketing compounds to valve cups. The largest is Handy Button Machine Co., with plants in Melrose Park, IL and New York, NY. They are said to produce about 1.2 billion units per year. Probably the next largest is the

Aeroclo Division of Precision Valve Corporation. Others include Bristol Flowed Gasket Co., Thomas Industries, Inc., and Sterling Seal Division. A few valve manufacturers also do some of their own pourings.

The other major valve mounting cup gasket is the "cut gasket", which in Europe is called the "laid-in gasket". It generally consists of a buna, neoprene or Viton hollow disc. Dimensions vary somewhat, but the i.d. is about 0.985" (25.0 mm) and the o.d. is roughly 1.142" (29.0 mm). The thickness was standardized in Europe about 1975, at 1.00 mm, or 0.039". In the U.S.A. a popular thickness has been 0.050" (1.27 mm). Gaskets down to 0.025" (0.64 mm) have been investigated, but below about 0.028" (0.71 mm) they become too flimsy for easy handling. Aluminum cans with "eyelashed curls" have seemed to require a gasket thickness of at least 0.036" (0.91 mm) to be quite free from radial micro-groove seepage.

An estimated 94% of the valves used in the U.S.A. and Canada use flowed-in gaskets, with cut gaskets being used only in particular product areas, such as some fumigants, many P-12 and P-114 refrigeration unit recharge cans, many of the larger diameter aluminum cans and a few other areas. Most valves in Japan and Australia used flowed-in gaskets. But in the rest of the world the most popular outer gasket is the laid-in type. An outstanding example is West Germany, where the ratio is 85% cut gaskets to 15% flowed-in gaskets, with valves being gassed by both T-t-V and U-t-C methods. In Europe, as a whole, it is estimated that about 60% of all valves carry the laid-in gasket, and that the percentage is steadily increasing. Originally the reason for using cut gaskets was the necessity to employ this type of seal to prevent the possibility of leakage in aluminum cans. Then it started to be used increasingly in the growing tinplate can market, because of its good performance and the problem of double inventories of both flowed-in and laid-in gaskets were to be maintained.

The cut gaskets are produced from smooth-surfaced, flat ground rubber sheeting by means of a cutting lathe or by punch presses. In at least one instance, this general type of outer gasket has been molded, more or less in the shape of the top third of a laterally sliced doughnut, with a crescent top and flat bottom cross-section. Producers include American Gasket & Rubber, Inc., Bentley Manufacturing Company, J.B.L. Corporation, Vernay Laboratories, Inc. and (in France) Le Joint Francais, S.A.

In the U.S.A. the most available laid-in gaskets include buna rubbers with Durometers of from 35 to 50, neoprenes with Durometers of about 65 to 85 and Viton fluoroalkane types. At least two Viton compositions are available. The most common is the brown type, generally 0.042" (1.07 mm) thick, but there is also a little-known black variety with a thickness of 0.035" (0.90 mm). The lower Durometer gaskets are much harder to handle on automatic placing machines, especially if they are relatively thin. In fact, one major valve manufacturer has standardized on an 80 Durometer buna in Europe, because of machine difficulties with lower Durometers and also with neoprenes. While laminated gaskets are very uncommon, sandwiches with low Durometer faces and high Durometer cores appear to have good machine handling properties, and the soft buna surfaces probably flow somewhat to make a still better hermetic seal with the valve cup arch and the can bead. At least a few million of these have been run with very good results. No blow-outs were encountered in U-t-C gassing tests.

Like the flowed-in gaskets, cut gaskets have rather complex compositions. They contain the basic polychloroprene, buna-N (polybutadieneacrylonitrile), or buna-S ingredients that characterize the gasket type, but in addition there are softening agents, age protectors, ozone protectants, lampblack, organic and inorganic fillers, curing and vulcanizing ingredients and so forth, according to the chemical and physical properties that are required. Factors such as tensile deformation resistance, low temperature set and module of elasticity can be adjusted according to the additives used. For example, a West German qualitative formulation for a black, oil-resistant gasket with a Shore A hardness of 75 is as follows:

- Perbunan N (Buna N)
- Zinc oxide - activated
- PAN aging protector
- Paraffin
- Lampblack (soot) - Durex
- Lampblack (soot) - CK
- Plasticizer
- Sulfur
- Vulcanizer CZ

In the optimum proportions, this composition gives a buna rubber with a typical tensile strength of 110 kg/cm², a breaking elongation of 360%, an impact elasticity of 43% and a density of 1.25. In these com-

positions it is important to minimize the free sulfur content, or bright machine finished aluminum can curls can be corroded, with the formulation of aluminum sulfide, Al_2S_3 .

In contrast to Europe, there is a significant lack of incentive to use cut gaskets in the U.S.A. The gaskets are not supplied already fitted to the valve cup and this process requires a hand labor operation. Then, in the hopper and sorter assembly of automatic valve inserter equipment up to about 1% of the assembled cut gaskets may fall out. If they are undetected, obviously a gross leaker will result when the unit is gassed. And finally, it is difficult to use U-t-C gassing equipment with these gaskets without blowing some of them into the can, again resulting in a gross leaker.

In the U.S.A. valves using cut gaskets are almost always gassed by T-t-V methods, since there has been little or no incentive to expand the technology. In Europe, T-t-V gassing was the standard method only until about the mid-1970s, but then, as the result of a special process said to have been developed by Precision Valve Europe, U-t-C gassing also came into widespread use. The basic technology is available from Precision, anywhere in the world, and it simply involves adjustments to the U-t-C gasser to establish a particular flow path for the propellant during charging. This optimum flow pattern results from strongly reducing the initial turbulent surge of gas-liquid into the container at the outset of the gassing phase. It is done by the use of needle valve flow controls, the use of relatively low propellant pressures, in the 400 to 600 psig (2.76 to 4.14 MPa) area, and by the use of sequential springs in the head.

Gasket Leakage Considerations

Valve leakage, through the crimped seal area, or through the seat or stem gasket area, has been the target of endless investigations. All aerosol dispensers leak to some extent, but those that leak excessively can bring about some serious commercial consequences. Ideally, leakage should not exceed about 0.1 Av.oz. (3 g) across a year of ambient temperature storage. Most aerosols fit into this category. Those that contain strong solvents, or sometimes those that have much higher pressures (such as CO_2 or N_2O packs), may leak at up to about 0.25 Av.oz. (7 g) per year. Any dispensers that exhibit leakage rates higher than this should be monitored very carefully. Perhaps the crimping dimensions were incorrect, or possibly the formulation could be

turned out just as well with lower percentages of strong solvents. A different elastomer might be required. These higher-leakage dispensers sometimes have the ability to hold the product well enough for several months, but after that period the seal may breach, allowing the can to depressurize in a day or two. These units are often called latent leakers and are unwittingly produced at the level of many millions each year.

The conditions of storage often have a considerable effect upon weight loss rates. Dispensers showing low weight loss rates in the upright position do not generally change materially if they are laid sideways or inverted. But if the formula contains a strong solvent, such as acetone, methylene chloride or toluene, or if it displays a moderately high weight loss rate in the upright position, then inversion can easily cause the rate to increase anywhere from about 20 to 100%.

Seepage rates almost always increase with increasing storage temperatures. As a very rough rule, when the storage temperature increases by 25°F (14°C), the rate of weight loss will increase by 50 to 100%. This generalization applies between 40° to 125°F (4 to 52°C). Many formulas with relatively large percentages of high solvent ingredients will function in a satisfactory fashion up to 100° or 110°F (38° to 43°C), above which they may eventually turn into latent leakers. The favored storage temperature for testing aerosol weight loss and compatibility is 100°F (38°C). This temperature will cover most field conditions and will promote a 50 to 100% acceleration of weight loss (over ambient temperatures found in the home). It will also act to speed up any corrosion or organoleptic problems, also by 50 to 100%, while still providing a valid qualitative relationship to room temperature effects. On the other hand, above 100°F (38°C), and particularly above 125°F (52°C), results may be obtained which would never occur at ordinary field temperatures. In one case, a water-based insecticide perforated a tinplate aerosol can in a week at 160°F (71°C), whereas packs stored at up to 100°F (38°C) showed almost no incompatibility, even after two years.

Table II (pages 158, 159) shows the effect of temperature, gasket selection and other factors on weight loss, using a very high solvency formulation based on 62% methylene chloride. When latent leakage took place, it generally occurred within four to eight months.

As a reference to the various crimp depths used in the table, it can be suggested that optimum dimensions would be those listed as follows on page 158.

GK-45 NVH gasket	0.178 ± 0.005 "
Water-based gaskets, as WDH	0.185 ± 0.005 "
0.042 " Viton gaskets	0.197 ± 0.005 "
0.050 " Buna and Neoprene gaskets	0.205 ± 0.005 "
0.014 " PE-sleeve gasket	0.182 ± 0.005 "

In this example depths were made on the low side of the specification or below it, recognizing the high solvent properties of the formulation.

A considerable body of knowledge has been assembled which suggests that the leakage rate through the mounting cup gasket seal is only 10 to 20% of the permeation loss through the stem gasket. One way to determine the leakage route(s) through an aerosol dispenser is to carefully gas a du Pont Dytel-12 solution into the formulation via the valve stem. This solution consists of a brilliant red dye in P-12. Any concentration can be added to the can, within headspace limitations. The can is then inverted and allowed to remain for a while until a red stain shows on the exposed area of the stem gasket or on the skirt of the valve cup. This will serve to pinpoint the site of leakage.

To determine the differential leakage rates between stem and cup gaskets a double eudiometer tube is used. This simple apparatus is shown in Figure 3.

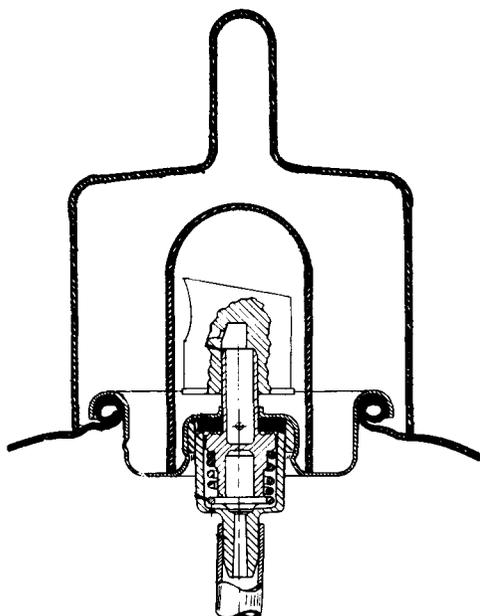


Figure 3. Cross Sectional View, Showing Aerosol Valve with Stem Gasket and Cup Gasket Eudiometers

Data for Table II on Facing Page

Pack	No. Cans	Valve	Cup Gasket	Stem Gasket	Crimp Depth
1	3	Seaq.	Cut buna	(Blind)	0.190"
2	3	Seaq.	Cut buna	.050" buna	0.190"
3	3	Seaq.	Cut buna	.050" neop.	0.190"
4	3	Seaq.	Cut buna	.042" Viton	0.190"
5	3	Grace	GK-45	(Blind)	0.175"
6	3	Grace	GK-45	(Blind)	0.185"
7	3	Summit	GK-45	.050" buna	0.175"
8	3	Summit	GK-45	.050" neop.	0.175"
9	3	Summit	GK-45	.042" Viton	0.175"
10	3	PVC	PE Sl'Ve	Buna 72A	0.175"
11	3	PVC	PE Sl'Ve	Buna 72A	0.185"
12	3	PVC	PE Sl'Ve	Neoprene	0.175"
13	3	PVC	PE Sl'Ve	Neoprene	0.185"
14	3	Seaq.	Cut Viton	(Blind)	0.190"
15	3	Summit	Cut Viton	.050" buna	0.190"
16	3	Summit	Cut Viton	.050" neop.	0.190"
17	3	Summit	Cut Viton	.042" Viton	0.190"
18	3	Summit	Latex 1809	.050" buna	0.175"
19	3	PVC	Latex WDH	.050" neop.	0.175"
20	3	Coster	(Flowed In)	Neoprene	0.180"
21	3	Grace	GK-45	(Blind)	0.185"
22	3	Grace	GK-45	(Blind)	0.165"
23	3	Summit	Cut Viton	.050" buna	0.185"
24	3	Summit	Cut Viton	.050" neop.	0.185"
25	3	Summit	Cut Viton	.042" Viton	0.185"
26	3	Summit	Cut buna	.050" buna	0.185"
27	3	Summit	Cut buna	.050" neop.	0.185"
28	3	Summit	Cut buna	.042" Viton	0.185"
29	3	Summit	1/2 GK-45	.050" buna	0.165"
30	3	Summit	GK-45	.042" Viton	0.165"
31	24	PVC	Latex WDH	Viton	0.165"
32	24	PVC	Latex WDH	Viton	0.175"
33	24	PVC	Cut buna	Viton	0.190"
34	24	PVC	Cut buna	Viton	0.185"
35	24	PVC	PE Sleeve	Viton	0.175"
36	24	Summit	Cut buna	Viton	0.180"
37	36	PVC	Latex WDH	Viton	0.167"
38	24	Summit	Cut Viton	Viton	0.190"
39	12	Summit	GK-45	Viton	0.175"
40	12	Summit	GK-45	Viton	0.165"
41	48	Summit	GK-45	Viton	0.170"
42	36	Summit	GK-45	Viton	0.170"
43	36	Summit	GK-45, low lined on cup	(Blind)	0.170"

TABLE II

Weight Loss Data for a Non-Flammable Aerosol Insecticide Product (g/yr)
 (3% Oils, 3% Isopropanol, 62% Methylene Chloride and 30% Propellent Blend A46)

Pack	Crimp Diam.	Weight Loss (77°F/yr)				Weight Loss (100°F/yr)				Weight Loss (120°F/yr)				No.	Gross Leakers %
		Upright aver.	max.	Inverted aver.	max.	Upright aver.	max.	Inverted aver.	max.	Upright aver.	max.	Inverted aver.	max.		
1	1.090"										5.51	5.92	0	0	
2	1.090"					25.78	26.35						0	0	
3	1.090"					18.66	19.34						0	0	
4	1.090"										6.90	7.40	0	0	
5	1.080"					empty	empty						3	100	
6	1.070"					empty	empty						3	100	
7	1.080"					30.68	31.46						3	100	
8	1.080"					21.92	22.57						2	67	
9	1.080"										7.40	8.01	0	0	
10	1.080"					26.98	33.91						3	100	
11	1.070"					34.38	37.24						3	100	
12	1.080"					18.65	20.68						2	67	
13	1.070"					29.99	31.74						2	67	
14	1.090"						2.30	2.97					0	0	
15	1.090"					21.25	21.94						3	100	
16	1.090"					15.67	16.29						0	0	
17	1.090"					6.50	7.90						0	0	
18	1.080"					23.84	24.25						1	33	
19	1.080"					16.00	17.52						0	0	
20	1.070"										16.73	27.08	1	33	
21	1.070"					0.91	1.24						0	0	
22	1.080"					empty	empty						3	100	
23	1.070"					37.40	39.00						3	100	
24	1.070"					25.49	26.93						1	33	
25	1.070"										6.12	6.42	0	0	
26	1.070"					31.49	32.35						3	100	
27	1.070"					23.42	23.96						0	0	
28	1.070"										10.80	12.14	0	0	
29	1.080"					28.49	30.25						3	100	
30	1.080"										empty	empty	3	100	
31	1.080"					4.66	6.44	5.17	6.85				0	0	
32	1.080"					4.39	6.06	4.87	7.22	empty	empty	empty	empty	-	-
33	1.090"					4.10	4.59	5.86	6.82	8.76	10.28	9.59	14.39	0	0
34	1.080"					5.05	9.04	6.49	8.65	10.41	12.52	13.49	15.59	0	0
35	1.080"					4.14	6.54	5.44	6.30	7.09	9.27	8.95	10.60	0	0
36	1.080"					4.00	6.28	4.62	4.86	7.91	9.48	8.45	8.81	0	0
37	1.080"	3.42	4.39	3.62	5.09	5.86	8.73	7.42	17.27						
38	1.090"					2.81	3.03	3.30	3.82					0	0
39	1.080"					5.13	7.28	6.26	10.34					0	0
40	1.080"					9.64	32.24	7.45	8.00					1	8
41	1.080"	4.07	4.62	6.51	12.82	5.15	10.94	7.63	20.01					0	0
42	1.080"	5.31	11.14	6.66	14.79	10.38	33.80	6.67	10.97	74.28	empty	16.77	46.87	5	18
43	1.080"	0.86	1.53	1.64	2.40	1.24	1.92	2.00	4.00	1.93	2.38	2.75	5.05	0	0

TABLE III
Typical Gasket Swell Levels After Immersion in Common Aerosol Solvents
 (Three days at 77°F - 25°C)

Solvent	Buna-N	Neoprene	Chlorobutyl	Viton A	EPDM	Polysulfide	Polyurethane
n-Hexane	1 ± 2	4 ± 2	40	0	26	0	4 ± 2
Ethanol - Anhydrous	1 ± 4	0 ± 2	-1	1 ± 1	-2	1	13 ± 8
Acetone	32 ± 14	7 ± 4	2	56 ± 12	-3 ± 3	8 ± 3	35 ± 7
Methylene Chloride	57 ± 22	35 ± 5	23	5 ± 3	9	53	40
Perchloroethylene	9 ± 8	32 ± 4	47	1 ± 1	32 ± 5	7	10

Courtesy of the FEA (Draft X-641)

Note: In five instances, out of 42, the figure or range denotes shrinkage. See interpretative limitations, as noted in text.

A more complete explanation of eudiometry is provided in the current Seventh Edition of the *CSMA Aerosol Guide*. In this instance, the twin tubes are pre-filled with water and are then placed over the valve pedestal and valve cup, respectively by holding the entire affair under water. After placement, the test unit is stored upright at ambient temperatures for two or three days, at which time the volumes of trapped propellant gas are noted. They may be calculated back into weight loss per year figures. Alternately, the weight loss of the dispenser can be determined over the testing period. If the can is assumed not to leak, or if it is a one-piece aluminum can, then the collected gas volume can be related to the weight loss, after which the stem gasket loss and the cup gasket loss can be determined readily.

Using combinations of methods such as these it has been found that the majority of valve leakage occurs through the seal between the top of the stem gasket and the opposing part of the pedestal. The usual causes are gasket variations, along with varying degrees of gasket compression when the stake is made to lock the valve components within the pedestal. The valve shown in Figure 2 is the Model SV-73 Vertical Action Valve by Summit Packaging Systems, Inc. and it has castellations on the upper part of the valve body that come up against the top of the pedestal. This mating of plastic against metal leaves a rather fixed vertical dimension for the stem gasket, so that compression will then relate almost solely to variations in gasket thickness. This design is viewed as superior to that of some other valve configurations. It should be noted that stem gaskets are typically 0.042 ± 0.005 " (1.07 ± 0.13 mm), which still leaves a lot of latitude for compressive variation, despite the fixed height of the gasket recess.

The compatibility between gasket and product has a profound effect upon weight loss. Products affect gaskets in a variety of ways. One of the most obvious is

swelling or (occasionally) shrinkage. There may also be leaching of certain additives, a breakdown of the polymeric structure and other degradative effects. Table III illustrates the short-term effect of five common solvents on seven elastomers, all of which have been used for either stem or cup gaskets at one time or another.

A number of limiting comments must be made in relation to Table III. They are as follows:

- a. Variations in swell for a given gasket type may relate to toughness, additives, Shore A or Durometer hardness and batch variations.

TABLE IV (Part 1 below, Part 2 on facing page)

All cans were 211 × 413 size; plain ETP inside.

All Viton stem gaskets were 0.042" (1.07 mm) thick.

Packs 4-C_a and 4-C_b were designed to check weight losses at the upper and lower edge of the crimp depth specification of 0.170 ± 0.005 " (4.32 ± 0.13 mm) of Pack 4-C.

M packs contain methylene chloride; C packs contain 1,1,1-trichloroethane.

Pack	No. Cans	Valve	Cup Gasket	Stem Gasket	Crimp Depth
1-M	60	PVC	Latex WDH	Viton	0.165"
1-C	36	PVC	Latex WDH	Viton	0.165"
2-M	24	PVC	Cut buna	Viton	0.190"
2-C	36	PVC	Cut buna	Viton	0.190"
3-M	24	PVC	Cut Viton	Viton	0.190"
3-C	36	PVC	Cut Viton	Viton	0.190"
4-M	36	Summit	GK-45	Viton	0.170"
4-C	84	Summit	GK-45	Viton	0.170"
4-C _a	12	Summit	GK-45	Viton	0.165"
4-C _b	12	Summit	GK-45	Viton	0.175"

- b. Swelling results will be different for other temperatures and time periods. If swelling is continuous with time, the gasket will eventually disintegrate. Some gaskets will swell for a few days and then shrink to well below the original size before reaching equilibrium.
- c. Gasket swelling in a mixture of two solvents cannot be predicted from a knowledge of the degree of swelling in each one, although it is generally within the range of values. Exceptions are found for mixtures containing the lower alcohols or water, where swelling may exceed the values for any single component.
- d. In about 90% of the tests the swell values at three days represented equilibrium states, but in some instances up to 21 to 28 days were required to reach equilibrium. In the case of neoprene stem gaskets used with a Choke and Carburetor Cleaner, the product was satisfactory at 28 days, but at between 36 to 48 days it started protruding out of the pedestal and causing gross leakage.
- e. Buna (nitron) sometimes shows a delayed frothing effect between gasket and stem due to very slow seepage. Although this may be unsightly, weight losses are small.

The inclusion of very small amounts of methylene chloride has sometimes been made to correct formulations showing either shrinkage or no effect on gaskets. In general, it is desirable to have from about 2 to 9% of swell, but swells over 10% should be viewed with some concern. On the other hand, cup gaskets seem to be more "insulated" from swelling problems than are stem gaskets, simply because of the crimp, and the fact that the elastomer just above the crimp is inhibited from swelling because there is no room for expansion without dislodging the seal, all the way around the valve cup. A good, extra-tight crimp is vital for susceptible gaskets to perform well in high solvency systems.

An example of this type of performance is given in Table IV, where several cup gaskets are compared with formulas that contain either 62% methylene chloride or 62% 1,1,1-trichloroethane but are otherwise identical. Viton stem gaskets were used since this material is known to give very low weight losses with chlorinated solvent formulations; see Figure 2, pack No. 25, and Figure 3, pack No. 3M and 3C. Although Viton gave the best results it is very expensive, commanding an up-charge of \$5.00/M or more for stem gaskets and about \$50.00/M for cut cup gaskets. It is not normally used if there are any alternates. (Butyl rubbers command similar premiums.)

TABLE IV

Comparisons of Weight Loss Between High Methylene Chloride and High 1,1,1-Trichloroethane Aerosol Insecticides

(3% Oils, 5% Isopropanol, 62% Methylene Chloride or 1,1,1-Trichloroethane and 30% A46)

Crimp Diam.	Solvent	Weight Loss (77°F (g/y))				Weight Loss (100°F (g/y))				Weight Loss (120°F (g/y))			
		Upright		Inverted		Upright		Inverted		Upright		Inverted	
		aver.	max.	aver.	max.	aver.	max.	aver.	max.	aver.	max.	aver.	max.
1.080"	CH ₂ Cl ₂	3.42	4.39	3.62	5.09	5.30	8.72	6.34	17.25				
1.080"	CH ₃ ·CCl ₃	1.33	1.80	1.35	2.38	1.54	3.07	2.05	2.79				
1.090"	CH ₂ Cl ₂					4.09	4.59	5.86	6.82	8.76	10.28	9.59	14.40
1.090"	CH ₃ ·CCl ₃	0.67	0.78	0.77	0.92	1.67	2.48	1.90	3.16	2.91	3.55	13.23	64.77
1.090"	CH ₂ Cl ₂					2.80	3.03	3.30	3.82				
1.090"	CH ₃ ·CCl ₃	0.29	0.49	0.33	0.45	0.53	0.90	0.51	0.92				
1.080"	CH ₂ Cl ₂	12.25	45.41	4.18	4.98	31.79	119.80	9.52	18.10	83.31	empty	47.69	63.55
1.080"	CH ₃ CCl ₃	1.11	2.07	0.99	2.49	2.20	31.88	1.55	4.35	1.89	2.43	1.85	2.53
1.080"	CH ₃ CCl ₃					2.01	2.75	2.56	4.20				
1.080"	CH ₃ CCl ₃					1.32	3.44	2.74	3.50				

Valve manufacturers recognize the importance of high quality gaskets to assure sealing integrity. One major supplier inspects 800 cups in every lot of 175,000 for gasket voids. This is a slug type defect, tending to begin suddenly and then die away rather quickly. At cup gasket thicknesses of below about 0.012" (0.3 mm) they are unavoidable. Finding one defect is cause for rejection and reinspection of the lot. The GK-45 NVH

thickness of 0.022 ± 0.007 " (0.56 ± 0.18 mm) with an AQL of 1.5 has now been both altered and tightened up considerably by several large marketers and valve makers. The most recent thinking suggests 0.025 ± 0.007 " (0.64 ± 0.18 mm) with an AQL of 0.10. The maximum single part variation is now 0.010" (0.25 mm). The so-called sidewall gasket (section) is either the usual 0.175 ± 0.015 " (4.45 ± 0.38 mm), AQL =

TABLE V

Nomenclature and Structure of Elastomers Used For Valve Gaskets

Tradename	Chemical Name	Polymeric Structure
Polyethylene, LDPE or PE-Sleeve	Polyethylene	$(-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_n$
(Various)	Polybutadiene	$(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_n$
Buna, Buna N, Perbunan-N, Nitrile or KP-6 Buna	Acrylonitrile-butadiene	$[(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_m-\text{CH}_2-\underset{\text{CH}_2}{\text{CH}}-]_n$
Buna S	Styrene-butadiene	$[(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_m-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-]_n$
EPDM	Ethylene-propylene-butadiene	$[-\text{CH}_2-\text{CH}_2-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_m-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-]_n$
Buna CB or Isoprene	Polyisoprene	$(-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2-)_n$
Butyl rubber	Isobutylene-isoprene	$[(-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2)_m-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2-]_n$
Neoprene, Perbunan-C or 759 Neoprene	Polychloroprene	$(-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2-)_n$
(Various)	Acrylonitrile-chloroprene	$[(-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2)_m-\underset{\text{CN}}{\text{CH}_2}-]_n$
Chloro-butyl	Isobutylene-chloroprene	$[(-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2)_m-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2-]_n$
Viton	Difluoroethylene-Hexa- fluoropropylene	$[(-\text{CF}_2-\text{CH}_2)_m-\underset{\text{CF}_3}{\text{CF}}-\text{CF}_2-]_n$
Thiokol	Alkyl-polysulfide	$(-\text{CH}_2-\text{CH}_2-\underset{\text{S}}{\text{S}}-\text{S}-)_n$
Vulkollen	Ethylenglycol-apidic acid-naphthalenediisocyanate polyester	(Variable)
Buna P	(Proprietary)	(Unknown)

0.25 below the cup curl, or now sometimes 0.171 ± 0.015 " (4.34 ± 0.38 mm) on the same basis.

Stem Gasket

The gasket surrounding the stem is possibly the most critical part of the valve assembly. It has to maintain a reasonable gas-tight seal even when flexed during operation of the dispenser. It also comes into contact with the product on all its surfaces, with the lower flat surface being in direct contact with the formula at all times. In the U.S.A. nearly all stem gaskets are made from either buna or neoprene. One major valve maker offers elastomers such as buna P, (slightly harder than regular buna N) according to the results of swell tests and other examinations. The composition of these gaskets is unknown. Viton stem gaskets are used to a vanishingly small extent because of price.

Neoprene stem gaskets are almost always supplied as low durometer stock, with a Shore A Durometer specification of 70 ± 5 . This same material is used for neoprene type seat gaskets for female valves. The specification is also standard in Europe. For instance, Metal Box Limited supplies neoprene only as "Neoprene 70" for their Metal Box Precision valves and Metal Box CL and CLF valves.

Buna N stem gaskets are available with Shore A Durometer specifications of 55 ± 4 , 65 ± 4 , 68 ± 4 , 70 ± 5 and 75 ± 5 , and perhaps others as well. However, most valve manufacturers have standardized on only one, two or at the most three, for their valves. The higher durometer specifications are sometimes preferred for high pressure (CO₂ type) formulations, as well as for high solvency compositions where their inherent toughness tends to inhibit swelling to some degree. Powder-containing products also work well with the higher range bunas. For example, a popular antiperspirant utilizes both 68 and 75 durometer material. Buna N stem gaskets are a popular item in Europe, where they are often called nitrile gaskets. They are available in the same durometer range.

The selection of stem gasket durometer is often dictated by the design features of the aerosol valve. For example, one popular valve in the U.S.A. and Europe can handle stem gasket durometers of from 55 to 70 and can be ordered with any gasket specification in the range. Others may not have this latitude. Spring compression, valve body design and other factors influence gasket selection.

Stem gaskets are made from other buna rubbers, from Viton, and sometimes from other elastomers. A greater diversity appears to be available outside the U.S.A. Table V provides a listing of some of the valve gasket materials that have been used, along with their polymeric structures.

Again, it must be recognized that each elastomer category contains specific compositions that vary widely in terms of additives, copolymer ratios, molecular weight distributions, degree of cross-linking and so forth. As an example of an obvious variation, both buna N and neoprene are available in white as well as black.

The white modifications are used mostly in the case of glass colognes and perfumes, where the container is transparent. A number of years ago, it was discovered that traces of lampblack carbon from black buna ferrule mounting gaskets were getting into alcoholic products and discoloring them rather significantly. The problem was eliminated by replacing the carbon with titanium dioxide or zinc oxide, although with a minor loss of engineering properties.

Stem gaskets are usually die cut from sheets or strips of material having a very smooth surface finish. The thickness is generally in the range of 0.040 to 0.050" (1.0 to 1.3 mm), with tolerances of from ± 6 to $\pm 12\%$, depending upon the supplier. The inside diameter relates to the geometry of the valve stem and is generally in the 0.096 to 0.148" (2.44 to 3.76 mm) range, with tolerances of from about ± 3 to $\pm 4\%$. The outside diameter also varies considerably with valve design but is often in the 0.375" (9.5 mm) area.

Not all gaskets are round. The Precision Valve Corporation has developed a unique "hex-gasket" with a hexagonal periphery for use with their spined cup & hex gasket very high speed T-t-V gassing valves. The mounting cup hole is ringed with six 0.040" (1.0 mm) round cut-outs, giving it a star-like appearance and facilitating extra-fast transfer of liquid propellant past the pedestal "barrier". Once inside the pedestal, the propellant can go past the depressed area of the stem gasket, between it and the valve stem, but also through six more-or-less chord-like apertures between the hex-gasket and the pedestal wall. The company recommends this valve for instantaneous T-t-V impact gassing and other applications, where extra-fast propellant injection can be beneficial. The valve can be either impact or liquistatically gassed at rates of from 0.5 to 1.5 seconds per unit, as a general rule.

Valve Stem

The stem is a hallmark of the male type valves. For the female types, the stem is usually made a part of the sprayhead. In the early years of the aerosol industry, stems were always made of brass or bronze, first as little pins and then, after about 1951, as regular hollow tubes with expanded bases, much like those that exist today. The brass stem survived until about 1957. Nylon stems, meanwhile, came into existence about 1952. As they were improved and the industry gained confidence in them, they almost totally displaced the more costly brass stems by about 1955.

The valve stem provides a metering orifice for the product, plus a channel to carry the material from the valve chamber into the actuator. It is either depressed or tilted sideways in order to operate the valve. The large foam-type valve stems or stalks made by the Clayton Corporation, Super-Whip Valve Manufacturing, Inc. and a few other firms do not require actuators. They dispense the product by a tilt-action principle from about an 0.125" (3.2 mm) hole at the end. Most stems are made of engineering plastics such as nylons or acetal, but for special applications they have been made of polyester or polyolefin plastics.

The orifice through the side of the valve stem is generally called the stem orifice or metering orifice. Using Laser beams, experimental stem orifices as small as 0.005" (0.13 mm) have been made, but they are highly subject to clogging and other problems. Production capability has been established for 0.010" (0.25 mm) stem orifices as a practical minimum diameter. Single metering orifices as large as 0.050" (1.27 mm) are known, as in the Seaquist PF-70 series valves, but usually they are not used above 0.025" to 0.030" (0.64 to 0.76 mm). At that point, it is often convenient to use a two, three or four orifice stem. One of the larger multi-orifice stems is the 3 × 0.050" (3 × 1.27 mm), but even larger sizes are being developed.

The valve stems with very large orifices are statistically more trouble-prone than other types. The vertical travel distance is somewhat increased, gasket deformation into the larger holes has to be considered, and of course the stem will be weakened at the orifice area to some extent. Since people are used to both toggle-acting and vertical-acting valves, they sometimes try to operate the vertical types as if they were toggles. This is especially true for starches and certain other products, where a high percentage of each valve type is in use. If a 3 × 0.050" (3 × 1.27 mm) or similar

stem is forcefully pressed at an angle, it may deform irreversibly at the orifice area or even crack.

Valve manufacturers have developed various mounting cup features that help protect vertical acting valves against this type of unintentional customer abuse. One of the earliest was developed about 1957, when customers misused a certain valve and caused it to spurt a bug killer up from between the stem and stem gasket seal. The top of the pedestal had been flat and the stem hole was larger than it needed to be. A new mounting cup design was offered shortly afterward, where the area near the stem was flanged upward and hugged the protruding stem.

In a few instances, the stem is also fitted with either an orifice or an orifice function at the top. For example, the Precision Valve Corporation 04-14 Series stem is equipped with a top metering slot of 0.011 × 0.016" (0.280.41 mm) size. The slot is readily accessible for cleaning and is used for paints and similar products in conjunction with PVC's 21-46 Series "Delta" actuator. In a second example, PVC uses a special 04-86 Series stem with their 01-87xx Series buttons in order to get a mechanical break-up (M.B.U.) action from a one-piece actuator. The deeply chamfered top section fits precisely into the mating area of the actuator and acts with it to provide the needed swirling action.

Some valve stems have a barb or molded-in lock ring around the periphery so that actuators, once attached to the stem, are almost impossible to pull off. For some products this can be an advantage. For example, in the case of highly lubricious products like silicone oils and penetrating oils, buttons might tend to pop off the stems after use, because of the momentary pressure still in the stem orifice and internal portion of the sprayhead. Many of these same product types sometimes act to swell the polyethylene or polypropylene buttons more than the nylon stem, exaggerating the problem.

A few stems are molded with unusual internals, such as a 0.040" (1.02 mm) chamber or a 0.030" (0.76 mm) post. These attributes lessen the volume inside the stem and reduce product afterspray and drool following shut-off at the stem metering orifice.

Whenever a ring-and-pad foam spout, partial or full diameter spray dome or other fitment is to be attached to both the valve stem and the rim of the valve cup, the question of relative stem height becomes important. *Stem height* is defined as the vertical distance from the top of the stem to the top of the arch of the mounting cup, after the dispenser has been filled, gassed and hot-

tanked. It is a function of the protruding length of the stem, known as stem extension, and the pedestal height relative to the top arch of the mounting cup.

Stem heights are influenced by the cup contour (flat or conical), the stem extension and the method of production. When a valve is crimped under ordinary conditions the stem height rises approximately 0.040" (1.0 mm). Adding pressure to the can causes a trace of upward pedestal distortion and stem gasket compression, totalling around 0.007" (0.18 mm); another 0.008" (0.20 mm) or so is added during hot-tanking. When the can cools back to ambient conditions, a relaxation of about 0.005" (0.13 mm) takes place. The result of all these increments is an overall stem height increase of about 0.050" (1.3 mm) during production.

Many valve suppliers offer valve stems in three or four lengths, plus the option of using either a flat or conical cup as a means of roughly matching the stem heights required by these special actuator fitments. The vertical difference between flat and conical cups is approximately 0.100" (2.54 mm), although this will vary with particular designs. In addition, the filler has the option of using "keepers" on his gassing equipment which act to limit the height of the pedestal and therefore the valve stem. With all these options, the filler can usually produce the desired stem height within about ± 0.020 " (0.5 mm). This is considered satisfactory.

Stem height is checked during production using either a "go/no-go" stepped gauge block or a special dial micrometer. Keeper adjustments may have to be made occasionally, if the range starts to drift significantly. The suppliers of foam spouts, actuator domes and other fitments should always be asked to stipulate the required stem height specification in writing, so that appropriate valve cups and stems can be selected for the development program.

Valve Body

For a male, vertical-acting valve, the basic function of the valve body (sometimes called the housing or the spring cup) is to provide an enclosure for the spring to force the base of the stem up against the valve stem gasket. It may also be provided with a tailpiece orifice and perhaps a vapor-tap orifice, and serves to make a connection with the dip tube. Valve bodies are generally molded of the same plastics as stems, using large, multi-cavity injection machines.

The tailpiece or main housing orifice extends from about 0.010 to 0.260" (0.25 to 6.60 mm) in diameter. In special cases there is no orifice as such, but large slots or channels, as in the Seaquist Valve Company NS-29 aerosol valve assembly, designed for bag or piston type dispensers. The larger orifices are designed for viscous products. In many cases, the dip tube is inserted into the tailpiece entryway and may or may not preempt the need for a tailpiece orifice. In the Seaquist NS-24 capillary valve assembly, any of six different capillary dip tubes may be inserted. The entry is chamfered for highly reliable machine insertion, and a circular barb or molded-in locking ring makes it almost impossible for the dip tubes to be separated. The capillary tubes have i.d.s of from 0.018 to 0.060" (0.46 to 1.52 mm) and can thus function as a lower or "tailpiece" orifice, if one is needed.

Vapor-tap orifices are used commonly to add a small amount of vapor phase propellant to the liquid stream, which acts to give a finer break-up, a lower delivery rate and a warmer spray. As an example, many antiperspirants use vapor-taps in order to reduce spray rates without reducing the other orifice sizes and taking the risk of clogging the valve with the aluminum salt. Vapor-taps are bored through either the body wall or the shoulder area near the base. They are either molded in or drilled by Laser to sizes which range from 0.010 to 0.030" (0.25 to 0.76 mm). Holes down to 0.005" (0.13 mm) have been made by Laser equipment but clog easily and in tests with whipped creams and certain other products did not seem to provide any significant benefit. Vapor-tap holes of 0.008" (0.20 mm) are probably available on a special order basis from some suppliers.

On some occasions, a vapor tap orifice is used in the reverse sense to provide a suitable spray with the dispenser in the inverted position. In this case, the body orifice becomes the vapor tap orifice. Feminine hygiene sprays often apply this principle. It is desirable to have both the tailpiece and vapor tap orifices about the same size, or the spray upon inversion of the container will be either faster or slower than that in the upright position.

Valve bodies have often been described as "regular" and "pressure-filling". In the past this meant that the regular valve was able to be gassed only at the rate propellant could pass through the valve stem and stem orifice(s), then through the body orifice(s) and into the can. If the valve stem orifice happened to be an 0.013" (0.33 mm) size, even at extremely high propellant pressures approaching 1200 psig (8.27 MPa), it would still