

[54] **PRESSURIZED DISPENSERS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 196,518, Nov. 8,
1971, abandoned.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**..... **B65d 83/14**

[58] **Field of Search**..... 222/399, 386.5, 192;
260/33.8 SB, 33.8 UA

[56] **References Cited**

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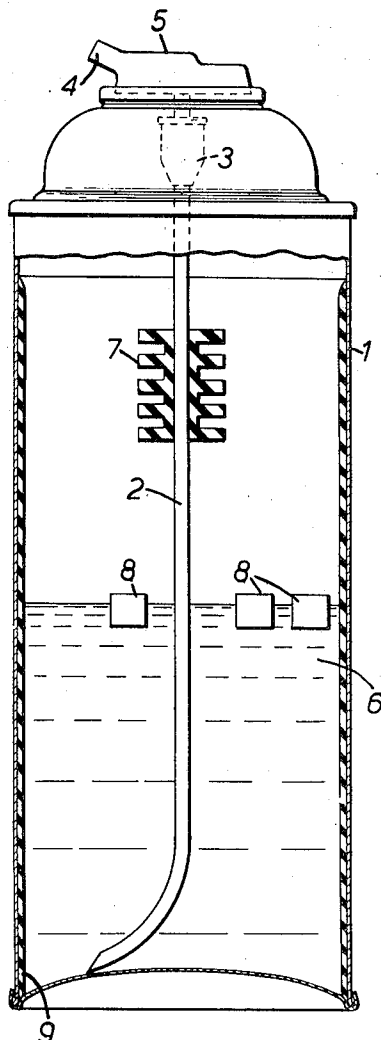
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[57]

ABSTRACT

As the contents of a pressurized dispenser are used up, the pressure within the dispenser container falls, resulting, for example, in the case of a foam dispenser in an undesirable change in the foam consistency, density and other properties. By the provision of a reservoir within the dispenser made of a substance capable of forming a solution with the propellant being employed, a controlled release of propellant in the dispenser is obtained as the contents are expressed to thereby maintain desirable foam consistency, density and other properties.

23 Claims, 7 Drawing Figures



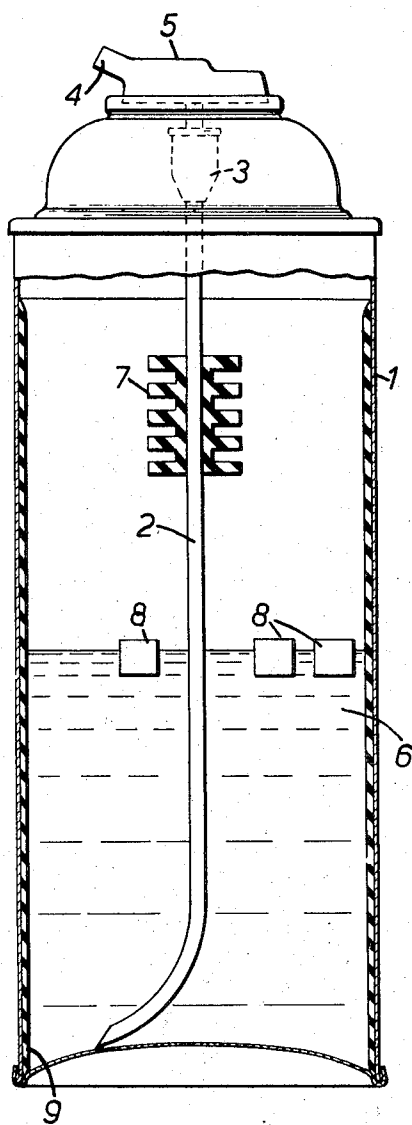


FIG. 1.

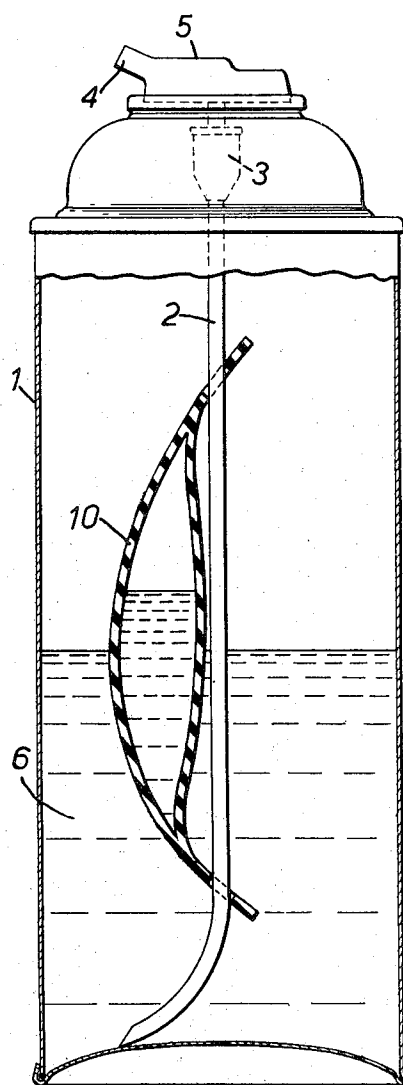


FIG. 2.

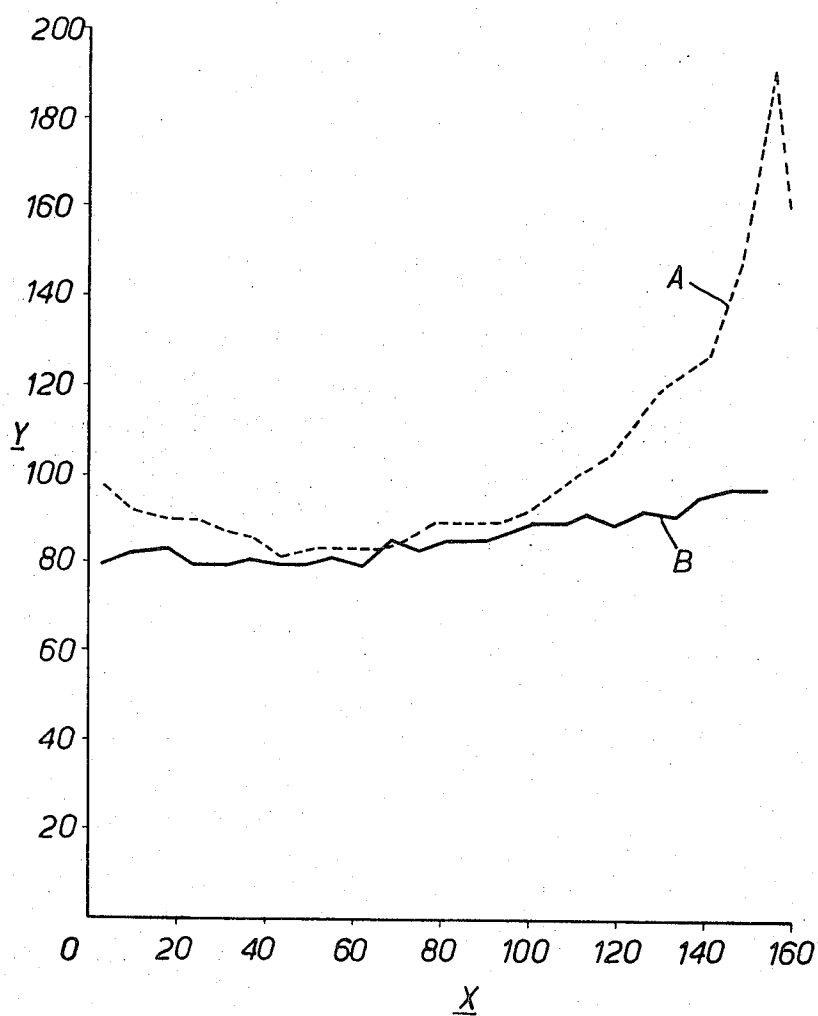


FIG.3.

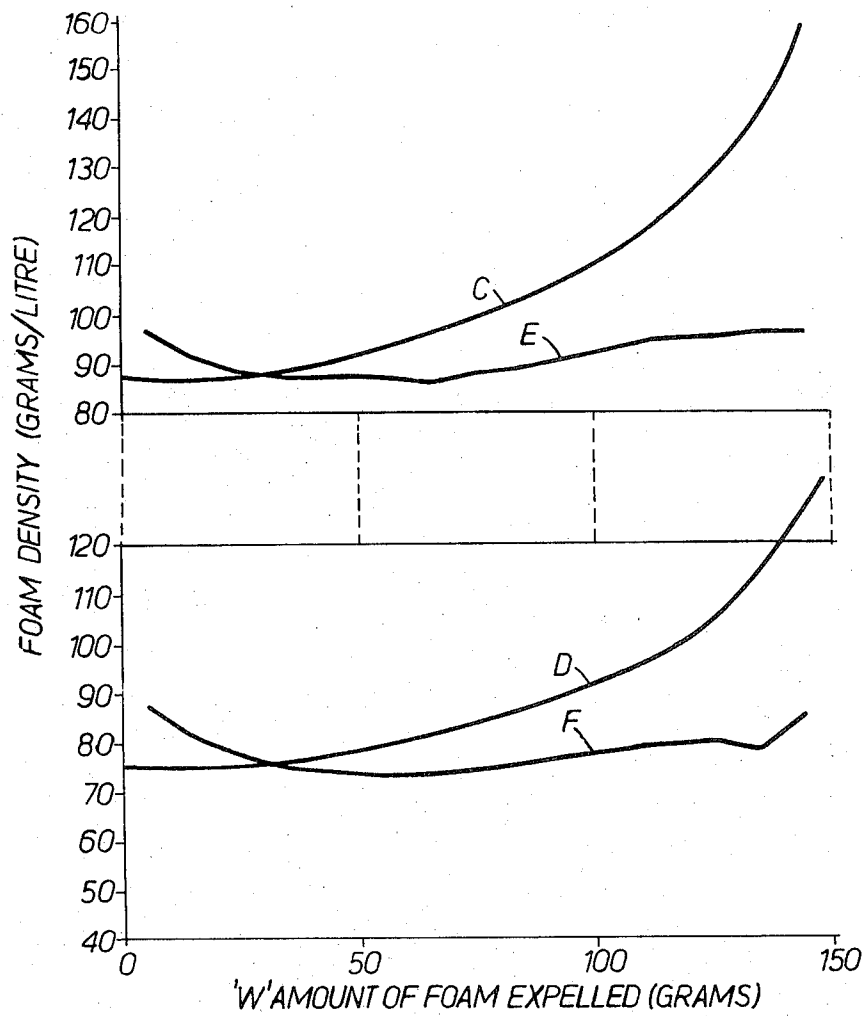


FIG. 4.

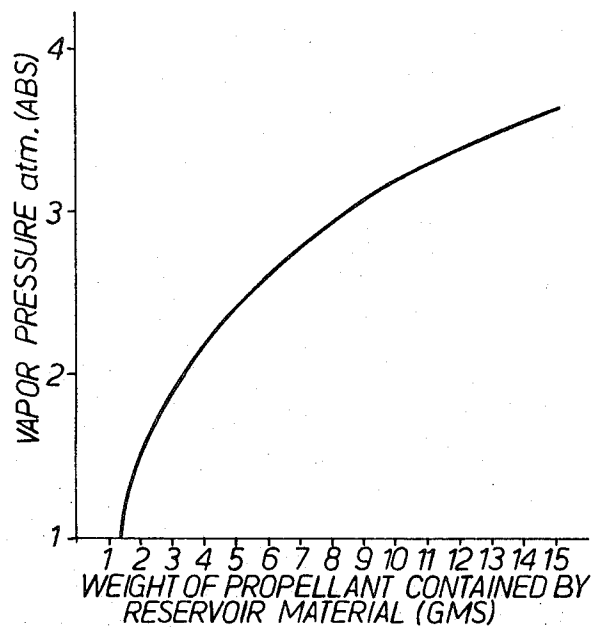


FIG. 5.

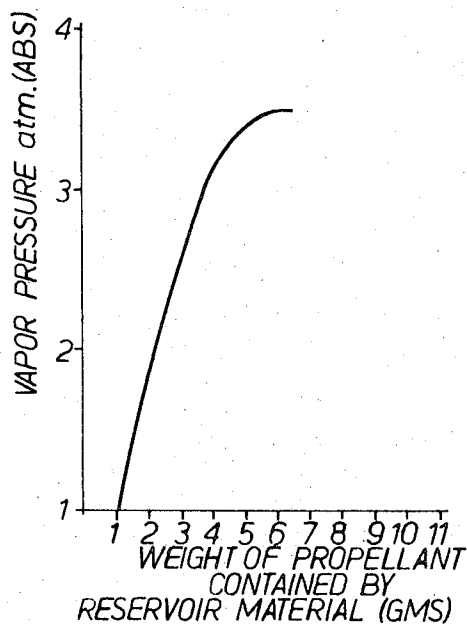


FIG. 6.

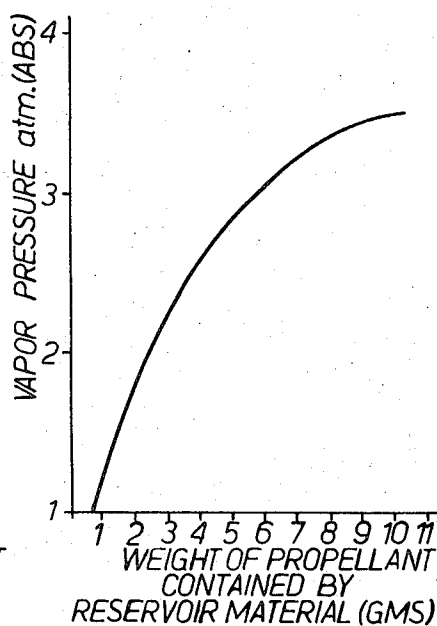


FIG. 7.

PRESSURIZED DISPENSERS**RELATED APPLICATION**

Watson, Ser. No. 196,518, filed Nov. 8, 1971, now abandoned, for: Pressurized Dispensers, of which the present application is a continuation-in-part.

This invention relates to pressurized dispensers such as aerosol containers and, more particularly, to pressurized dispensers characterized by improved performance.

When using aerosol containers to dispense a liquid concentrate mixed with the propellant in the dispenser container so that part of the propellant is discharged with the concentrate and part evaporates into the head space above the liquid mixture to provide the driving pressure, the ratio of the propellant to the liquid concentrate in the mixture falls as the contents of the container are dispensed. This is caused by the loss of propellant as gas to the head space as the head space volume increases due to the contents of the container being expressed. When a foam is being dispensed, this reduction in the ratio of propellant to concentrate increases the density of the dispensed foam; and a runny product can and often does result. This effect of accelerating depreciation could be alleviated by initially adding more propellant, but the increased initial propellant to concentrate ratio would result in an undesirably low initial foam density.

Regarding the dispensing of dry products such as talc, the problem involved is to isolate the liquid propellant from the dry powder product within the dispenser container to avoid wetting of the powder. While this problem can be overcome by dividing the interior of the container into compartments, this expedient is relatively expensive from the commercial standpoint.

It is an object of the present invention to provide a pressurized dispenser including a supplemental source of propellant capable of releasing propellant into the system as additional propellant is required for performance. A related object provides such a pressurized dispenser which can be filled with propellant without the necessity of modifying conventionally used filling procedures.

A further and more specific object of this invention lies in the provision of a pressurized container for dispensing concentrates mixed with liquid propellant which allows the concentrate-propellant ratio to be maintained within acceptable limits throughout the life of the container.

Another specific object provides a pressurized foam dispenser characterized by the ability to dispense foams with more uniform properties such as density, viscosity, lubricating properties and the like.

Yet another object lies in the provision of a pressurized dispenser capable of dry products in a reliable fashion without wetting of the product with propellant. A related object provides a pressurized dispenser having the ability to dispense a dry product without any detectable chilling effect of any significance.

A still further object is to provide a method of charging supplemental propellant to a pressurized dispenser.

A further object provides a pressurized dispenser for aqueous products in which any significant emulsification or other adverse association of the propellant with the aqueous product being dispensed is avoided.

Another object of the present invention is to provide a method of reducing the pressure of an aerosol system without recourse to admixture with expensive low-volatile propellants.

A still further object lies in the provision of a pressurized dispenser characterized by the ability to function satisfactorily even when the headspace propellant gas has been discharged accidentally.

Yet another object provides a system which may be utilized to provide a liquid-free, gas stream of solely propellant for, as an example, a Venturi-type spray.

Other objects and advantages of the present invention will become apparent as the following description proceeds, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a cross sectional view and illustrating a pressurized dispenser including various embodiments of propellant reservoirs in accordance with the present invention;

FIG. 2 is a cross sectional view and showing a pressurized dispenser or aerosol dispenser according to another embodiment of the present invention;

FIGS. 3 and 4 are graphs of the density of foam dispensed from an aerosol dispenser versus the amount of foam expelled and demonstrating the effectiveness of employing a pressurized dispenser having a reservoir in accordance with the present invention, and

FIGS. 5 through 7 are graphs illustrating, for exemplary reservoirs in accordance with the present invention, the relationship between the amount of propellant held by the reservoir and the vapor pressure within a pressurized dispenser.

While the invention is susceptible of various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and will hereinafter be described in detail. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the invention as expressed in the appended claims. Thus, the specification provides a description of a wide variety of materials that may be suitably used to form the reservoir of the present invention. It should be appreciated that the types of materials illustrated are only exemplary, and it is within the scope of this invention to use any material for the reservoir which is capable of functioning in accordance with the criteria for the reservoir which will be described herein. In addition, while the specification describes the present invention using certain aliphatic and halogenated hydrocarbons as propellants, it should be understood that the invention is also applicable to other propellants. As representative examples of useful propellants, satisfactory organic propellants include aliphatic hydrocarbons and partially or fully halogenated hydrocarbons having vapor pressures in the range between about 5 pounds to about 200 pounds per square inch gauge at 70°F. or mixtures of two or more such compounds which in the combined mixture provide a vapor pressure within the ranges herein set forth. Indeed, the present invention may be desirably employed in connection with a mixture of an organic propellant with an inorganic propellant such as, for example, nitrogen. Also, while the invention is generally described in connection with the dispensing of foam products or dry products, it should be similarly appreciated that the

present invention may also be used in connection with systems having only a gaseous phase, liquid concentrates such as hairsprays in which the propellant is typically dissolved in the liquid, aqueous concentrates wherein the propellant is a separate phase such as aqueous insecticides, and solid products dispersed in a liquid which is primarily the propellant such as certain liquid antiperspirants. It should be further understood that the use of the present invention in the various types of pressurized dispenser systems described herein will not necessarily yield the same benefits. For example, when used with a system containing a high proportion of propellant such as a hairspray, the sole benefit of employing the present invention may be an economic one.

Briefly, the present invention provides a pressurized dispenser comprising a container provided with a valve-controlled outlet and containing a concentrate (viz., the total dispensable contents of the container, other than propellant) to be dispensed and a reservoir formed of an organic substance (e.g., rubber) holding the propellant in solution. The reservoir is solid or is enveloped in a solid material so that it is retained in the container as the concentrate is being dispensed. By the term forming a "solution" with the propellant, it is meant in this specification that the claims that the vapor pressure over the propellant dissolved in the reservoir is less than that of the pure propellant. The propellant held in solution in the reservoir is capable of being released as the equilibrium within the container is upset by the dispensing of concentrate to provide a supplemental source of propellant to improve the dispensing function.

The weight of the reservoir material employed is determined by the amount of the propellant that the reservoir must release to achieve the desired improvements in performance. The amount of propellant which can be released is in turn related to the amount of propellant that the reservoir material can hold in solution. To be useful, at least from the standpoint of economy, the organic material forming the reservoir should be capable of forming a solution with at least 15 percent of its own weight of propellant at room temperature. The amount of propellant necessary is, of course, also dependent upon the type of propellant or propellants used as well as the predetermined initial and the lowest acceptable final pressure of the particular dispensing system.

Turning now to the accompanying drawings, FIG. 1 shows a conventional form of an aerosol foam container in cross section including a reservoir in accordance with the present invention. As is illustrated, the aerosol foam container comprises a pressure-resistant can 1 having a dip tube 2 extending downwardly to the bottom of the can from a valve 3 which controls the flow to a nozzle 4 and is itself controlled by a finger-operated button 5. Within the can 1 is a liquid mixture 6 comprising a propellant and a concentrate such as, for example, a shaving foam consisting of a strong solution of soaps. It should be understood that the particular construction of the container, valving and dispensing equipment does not form a part of the present invention, and the illustrative embodiment is only exemplary.

In accordance with the present invention, to provide a source of supplemental propellant as the concentrate is dispensed, there is provided a reservoir holding pro-

pellant in solution and capable of releasing propellant as concentrate is dispensed. The physical form which the reservoir will assume will vary according to the material from which the reservoir is made, and also as to whether the reservoir is assembled by the container manufacturer, the valve manufacturer, or the packager filling the container. As shown in FIG. 1, for a valve manufacturer, the reservoir can be formed as a single mass 7 mounted tightly on the dip tube 2. Similarly, the reservoir could assume a tubular shape and be held on the dip tube by a retaining pin or could be attached to the valve body itself. For a packager, the reservoir could desirably assume the shape of a number of discrete masses 8 or as a rubber rod. When the reservoir is to be assembled by the can manufacturer, the reservoir could be formed as a continuous coating 9 or a series of spaced strips on the inside wall of the container 1. As a still further alternative, one or more of the components of a container, such as for example the dip tube or valve, could be made at least in part from one of the reservoir materials. In yet another alternative, the reservoir can be formed as a continuous coating or as a series of spaced strips on the inside wall of the dome of the container.

In all instances, the main criterion is that the physical form of the reservoir and its positioning within the container should not interfere with the operation of the dip tube or valve. The reservoir should also desirably have a sufficiently large surface area and thin cross-section to allow accelerated dissolution of the propellant in the reservoir material as well as subsequent release of the propellant from the reservoir. However, if the concentrate is a viscous liquid, it may be desirable to avoid a very large surface area reservoir since concentrate which would be otherwise available could thereby be lost by adhesion to the reservoir.

The type of organic materials which may suitably be employed for forming the reservoir varies widely. The principal criterion is that the material must be capable of holding the propellant in solution, as opposed to merely absorbing propellant into the pores of the material in which case the propellant remains in the form of the pure liquid propellant. By being held in solution in the reservoir, the vapor pressure of the dissolved propellant over the reservoir is reduced below that of pure propellant. In the case of a liquid concentrate mixed with liquid propellant, when the concentrate is dispensed, thereby upsetting the equilibrium in the container, propellant from the reservoir can then release to establish a new equilibrium. The pressure in the system is thus greater than would have resulted in a container not possessing the reservoir of the present invention.

Considering this further, since the vapor pressure above a propellant-concentrate solution within a pressurized dispenser is also reduced below that of the pure propellant, propellant can and will transfer from the propellant-concentrate solution to the reservoir, or vice versa, until equilibrium is established. This transfer can, of course, take place directly where there is contact between the reservoir and the propellant-concentrate solution, or by distillation via the head space when the reservoir is located in the head space. The increasing head space within the container caused by dispensing concentrate will thus cause propellant to evaporate either from the reservoir or from the propellant-concentrate mixture, or from both, until the extra head

space has been filled; and equilibrium has once more been established.

In addition to the above requirements, the material used for the reservoir should be inert to the product being dispensed to avoid contamination and not break up after forming the solution with the propellant so that the operation of the dispenser (e.g., blockage of the valve) would be impaired. Further, it is desirable that the material not produce any off-odor in the dispensed product. It is also important that the reservoir material should not absorb, dissolve or otherwise remove any component of the concentrate to an extent which would cause the dispensed concentrate product to be significantly changed in character.

While many organic materials are capable of dissolving and releasing propellant, and hence could be used to form the reservoir, as has been stated, economics generally dictate that the reservoir material should be capable of forming a solution with at least 15% of its weight of propellant when in contact with the liquid propellant or its saturated vapor at room temperature. However, what is important is the amount of dissolved propellant that can be released; and such organic materials will typically also be capable of releasing a significant proportion of the dissolved propellant as the vapor pressure of the propellant in a pressurized dispenser falls to 60 percent of its initial value. By a "significant proportion" it is intended to mean that the material is capable of releasing at least an amount of propellant equal to 5 percent of the weight of the organic material. What is required to achieve the desired increase in dispensing performance in a specific instance may well, however, be in excess of the 5 percent amount referred to herein. As will be seen hereinafter, the present invention discloses various reservoir materials which are capable of releasing propellant under the conditions described in an amount which is substantially in excess of the 5 percent minimum figure which has been re-

preferred to use such rubbers with foams typically when fluorocarbon propellants are being used. There is typically little or no tendency for these prevulcanized latex rubbers to flow on forming a solution with the propellant. Unvulcanized latex rubbers are about as effective as the prevulcanized materials but tend to flow and absorb concentrate. Thermoplastic rubbers tend to soften with use with butane-type propellants, but suitable grades are available which will allow satisfactory use with such propellants. Butyl rubbers are usable in an unsupported manner and are chemically very inert; however, the rate of equilibration may be too low for use with fluorocarbon propellants.

In addition, SBR, isocyanate (e.g. a casting mixture from hydroxy-terminated polybutadiene and toluene di-isocyanate), ethylene/propylene, polyisoprene (synthetic) and ethylene/vinyl acetate rubber may also be used. Also, mixtures of rubber may be employed. Thus, blends can be employed or an admixture of particles of one rubber (e.g., less than 2 mm. in dimension) in a matrix of rubber. By using such a dispersion, improvement in the effective dimensional stability (viz., from the dispersed rubber), can be achieved while retaining good absorbing properties for the propellant. Also, a rubber of superior absorbing properties may be utilized in a matrix of a casting mixture (e.g., the isocyanate rubber previously described) or a molding rubber (e.g., a "Cariflex" thermoplastic rubber, Shell Chemicals, Ltd., London, England). In such an embodiment, the composite material forming the reservoir may be molded directly onto a container component or directly onto the inside of the container wall or dome.

The amount of propellant dissolved at saturated vapor pressure gives a useful guide to the amount released during a pressure drop. Table I demonstrates the performance of some commercially available rubbers or elastic polymers which are representative examples of materials suitable for use in forming the reservoir.

Table I

Samples of Rubber	Weight (gm.) of propellant dissolved by 100 grams of rubber at room temperature, saturated vapor pressure.				
	Butane 40	Propellants 11	12	114	40/60 12/114
Sample A	170	380	450	350	350
Sample B	61	370	68	21	36
Sample C	92	600	82	36	51
Sample D	155	Disintegrates	84	37	49
Sample E	90	Liquifies	148	23	50
Sample F	Liquifies	Liquifies	80	14	51
Sample G	61	Not measured	Not measured	Not measured	33

ferred to and is more than ample to provide the desired improvements in dispensing performance.

Suitable organic materials which have been found to be useful for forming the reservoir include various rubbers such as silicones, prevulcanized natural rubbers, unvulcanized natural rubbers, polyisobutylene rubbers and thermoplastic rubbers made by the block copolymerization of isoprene and styrene, or butadiene and styrene.

Silicone rubbers equilibrate particularly rapidly and have been found to be efficient for use with fluorocarbon propellants and with foam concentrates. These rubbers generally have little or no tendency to flow on forming solutions with the propellant. Prevlcanized natural latex rubbers can be effectively used with both fluorocarbon and butane propellants; however, it is not

The propellants referred to in Table I are defined as follows:

Butane 40 which is a mixture (by wt.) of 22 percent propane, 24 percent isobutane and 54 percent n - butane;

Propellant 11 which is trichlorofluoromethane;

Propellant 12 which is dichlorodifluoromethane;

Propellant 114 which is symmetrical dichlorotetrafluoroethane. This can be used by itself or, for example, in a 40/60 percent mixture (by wt.) of propellant 12 and propellant 114.

The rubber samples referred to in Table I may be described as follows:

Sample A is a translucent silica-filled grade of "TC156" silicone rubber, commonly used for labora-

tory and surgical equipment. (Esco, Ltd., London, England), having the following typical properties: tensile strength — 925 to 1,100 P.S.I., elongation at break — 350 to 400 percent, brittle point, — 62°C., tear strength 9–12 lbs., and hardness 45–55 BS°. Sample B is a lightly vulcanized composition containing 75 percent of a high grade natural rubber. Sample C is a lightly cross-linked hydrocarbon rubber prepared from "Dunlop A330" prevulcanized natural rubber latex (Dunlop Chemical Products Division, Birmingham, England) containing 61 ± 1 percent solids. Sample D is a rubber sheet material prepared from "Dunlop A390" unvulcanized natural rubber latex containing 54 ± 1 percent solids. Sample E is a "Cariflex 1107" thermoplastic rubber (Shell Chemicals, Ltd., London) made by block copolymerization of isoprene and styrene, having the following indicated properties: at 23°C., tensile strength (ASTM D412-64T) — 250 Kg. 1cm.² (dumbbells cut from films cast from toluene, 20 percent by weight); modulus, 300 percent — 8 kg./cm.², elongation at break — 1,300 percent hardness (Shore A) — 35, viscosity of a 5 percent solution by wt. in toluene — 20 cps. and a 25 percent solution in toluene — 1,800 cps (Brookfield viscometer, 23°C.). Sample F is "Oppanol B 100" polyisobutylene, of viscosity-determined average molecular weight 1,300,000 (B.A.S.F. Ltd., London). Sample G is "Cariflex 1,101" thermoplastic rubber made by block copolymerization of butadiene and styrene (Shell Chemicals, Ltd.), having the following properties: tensile strength (23°C.) — 325 kg./cm.², modulus 300 percent — 30 kg./cm.², elongation at break — 880 percent, viscosity of 5 percent solution by wt. in toluene is 3.5 cps. and of a 25 percent solution is 6,000 cps. (Brookfield viscometer, 23°C.).

Whether a particular material may be satisfactorily employed for use in forming a propellant reservoir in accordance with the present invention depends on factors such as the type of propellant used and the amount of propellant with which it will form a solution. While unvulcanized natural rubbers can be desirably employed to form satisfactory reservoirs with butane propellants or a dichlorodifluoromethane propellant, the use with a propellant such as trichlorofluoromethane can either result in a flowable reservoir or a reservoir which is mechanically insufficient, from a strength standpoint, to withstand normal usage in a pressurized dispenser.

Natural rubbers can be partially vulcanized as a latex to form a prevulcanized latex, the vulcanizing being carried out in such a fashion that further vulcanizing does not occur upon drying the latex (viz., containing, for example, only about one cross link per 500–1000 carbon atoms). Such partially vulcanized rubbers are well known in the art. In general, such prevulcanized natural rubber materials form solutions with propellants that are mechanically more suitable for use in pressurized dispensers than solutions of the corresponding unvulcanized natural rubbers. However, prevulcanized natural rubbers may form saturated solutions containing less propellant than do corresponding weights of unvulcanized natural rubbers, particularly when used with hydrocarbon propellants.

Particularly satisfactory mechanical strength can be achieved for reservoirs by using unvulcanized natural rubber mixed with a prevulcanized natural rubber. This can allow retention of the particularly good solution-forming properties of the unvulcanized natural rubber.

Indeed, with certain propellants, as, for example, a 40/60 percent mixture of dichlorodifluoromethane and symmetrical dichlorotetrafluoroethane, mixtures of such unvulcanized and prevulcanized natural rubbers not only provide reservoirs having satisfactory mechanical characteristics; but the weight of propellant in the resulting solutions can be higher than the same propellant with either the unvulcanized or the prevulcanized natural rubber alone. As one example, enhancement of propellant content in the reservoir can be achieved with mixtures containing from 50 to 70 percent by weight of prevulcanized natural rubber, based on the combined weights of the unvulcanized and prevulcanized natural rubbers. A weight ratio of about 1:1 has been found particularly advantageous for forming solutions with the 40/60 percent fluorocarbon propellant mixture previously identified.

When using vulcanized synthetic rubbers derived from isobutylene, it is preferred to formulate the isobutylene rubber with a small amount (e.g., up to 5 percent, generally from about 2 to 3 percent by weight) of a further monomer which when copolymerized will produce a polymer that can be vulcanized. Suitable monomers include isoprene, butadiene and chloroprene. "BUTYL X X" vulcanized isobutylene-based synthetic rubber (ESCO, Ltd.) has been found to be particularly useful for forming reservoirs with trichlorofluoromethane propellant.

Unvulcanized polyisobutylene rubbers are also useful. The physical properties of solutions of such rubbers with propellants will typically vary depending upon the particular propellant. The average molecular weights of the rubbers will also influence the physical properties of the solutions, and such rubbers should generally be selected at least such that the desired solution with the intended propellant does not flow under its own weight. Satisfactory reservoirs have been formed with various unvulcanized polyisobutylene rubbers and propellants such as butane, dichlorodifluoromethane, and a mixture of dichlorodifluoromethane and symmetrical dichlorotetrafluoroethane (40:60 by weight, respectively).

If it is desired to strengthen the shape of the reservoir, this can be achieved by the incorporation of structural fillers. The filler can suitably comprise either a material, inert to the propellant, or an organic material usable itself to form a reservoir but which is less deformable than the primary reservoir material. Any of the fillers known in the rubber art to impart increased dimensional strength may be used. Silica, zinc oxide and carbon black are illustrative examples. Typically, the inclusion of fillers will not modify the ability of the rubber to form a solution with a given amount of propellant.

In addition, the rubber materials forming the reservoir may be advantageously extended with small quantities of a non-volatile oil (e.g., mineral oil) or a low melting solid (e.g., a paraffin wax). Such extended rubber formulations often effectively increase the amount of propellant which will be dissolved by a given weight of rubber as well as accelerating equilibration times. Depending upon the particular rubber, such inexpensive extenders may be employed in amounts up to about 15 percent by weight of the rubber. It should be understood that such additions are not desirably utilized in systems where they might leach out from the rubber of the reservoir. Thus, leaching might occur

when a foam concentrate is being dispensed; but use with dry powders would be acceptable since leaching of the oil or the like from the rubber is unlikely.

To supply the propellant to the reservoir, the charge of the concentrate to be dispensed and the propellant may be first introduced into the container with an excess of the propellant being included. The reservoir material will then gradually dissolve the excess of propellant until an equilibrium is established.

Alternatively, the reservoir material can be charged with propellant externally of the container and then introduced into the container before or after the concentrate. This mode is particularly desirable when the concentrate is a powder which should not come into contact with liquid propellant.

The time required for the reservoir material to come to equilibrium with the particular propellant being employed varies considerably. It is of course, important to know what the rate is so that the propellant-reservoir material will substantially achieve equilibrium prior to the time of use. The time needed to reach equilibrium may also vary depending upon whether the reservoir material is charged by immersing in the liquid propellant, is suspended in propellant vapor or is immersed in the liquid concentrate being dispensed. It has been found that the time required to reach equilibrium varies from between about one day to three months.

The weight of the reservoir material which should be used depends on several factors. The weight of the reservoir will, of course, be determined by the weight of the concentrate to be dispensed. The amount of propellant with which the reservoir material can form a solution and the amount of dissolved propellant which will be released as the head space in the container increases are also important in determining the reservoir weight that should be used. In general, in usage in pressurized dispensers, a rubber reservoir will typically release at least one-half, usually two-thirds, of the propellant with which it is capable of dissolving at the saturated vapor pressure of the rubber. Illustrative examples of rubber materials for reservoirs in accordance with this invention which combine economy with satisfactory functional advantages, per 100 grams of a shaving foam concentrate, are as follows: prevulcanized latex rubber, 4 gms. plus 3 gms. additional hydrocarbon propellant; prevulcanized latex rubber, 6 gms. with 4 gms. of additional fluorocarbon propellant; silicone rubber, 3 gms. with 5.0 gms. of additional fluorocarbon propellant; thermoplastic rubber, 6 gms. plus an additional 4 gms. of hydrocarbon propellant.

For powder products, the weight of the rubber reservoir should be selected so that all of the contents may be satisfactorily expelled during use. Ideally, the rubber reservoir is charged with propellant until the pressure in the system at equilibrium is such that, during a drop in temperature that might occur in normal household storage conditions, no propellant will condense as a liquid in the system. As an example, a six-ounce container of a product dispensing talc product will be expelled by a hydrocarbon propellant dissolved in 25 gms. of a reservoir formed of a prevulcanized rubber.

In the embodiments discussed above, the reservoir comprises a material which does not flow, viz., the reservoir having been swollen by the propellant and submitted to conditions of normal usage will return to substantially its original dimensions if it loses all its propellant. According to a further aspect of the present inven-

tion, organic materials which form mobile solutions with a propellant may also be used. To this end, the mobile propellant-reservoir system is retained within a capsule, the walls of which are readily permeable to the propellant but not to the reservoir material. This also allows the use of organic substances that are liquids or semi-liquids under the conditions of usage.

When choosing the capsule wall material, the main requirement is that a material must readily transmit propellant at normal working temperatures. A transmission rate of the order of about 0.1 gm./dm.²/hr. at room temperature is satisfactory. A representative example of a suitable capsule material is a low density polyethylene film of about 0.005 inch thickness (molecular wt. — up to about 50,000 — specific gravity of 0.915–0.940 and melting point of 109°–125°C.) The organic material serving as the reservoir must be selected so that it will diffuse through the capsule wall considerably less readily (e.g., having a transmission rate of less than about 0.05 gms./m.²/day) than the propellant. For use with a capsule formed of low density polyethylene, a mobile polyisobutylene or a microcrystalline wax may be employed. Polyisobutylenes having a viscosity average molecular weight of about 50,000 to 100,000 and a number average molecular weight of about 8,000 to 13,000 are exemplary of satisfactory materials. Suitable examples of microcrystalline waxes, formed by the chilling of a petroleum distillate and containing a large proportion of branched chain and saturated ring molecules with some long chain hydrocarbons (40 to 60 carbon atoms, molecular wt. — 580–850), are those which will exhibit melting points within the range of 60°–70°C.

As an illustrative embodiment, FIG. 2 shows a container wherein the reservoir is contained within a capsule. For sake of simplicity, the same components of the pressurized dispenser and valve assembly have been given the same numerals as in FIG. 1. However, the organic reservoir material is retained within a capsule or sachet 10 formed, for example, from low density polyethylene. The capsule 10, as illustrated, is secured to the dip tube. The capsule can be loose within the container, if desired.

The following examples are further illustrative of the present invention but should not in any way be considered in limitation thereof. Unless otherwise specified, all percentages are by weight.

EXAMPLE 1

A shaving foam was prepared as follows. Into a 220 ml. tin-plate container was placed 150 grams of concentrate having the following composition: stearic acid 4.5 percent; lauric acid 4.0 percent; triethanolamine 3.5 percent; "PCL liquid" emollient oil (a mixture of alkyl-branched fatty acid esters with a low solidification point, –4°C. to 1°C., refractive index n_D^{20} 1.444–1.446 and an ester number of 135–160, 4 hr. saponification; Dragoco Ltd., Suffolk, England), 2.5 percent lauryl ether sulphate 0.4 percent; water to 100 percent. The can was purged and with the valve secured in position, propellant 12/114 (40:60 ratio), 14.0 grams was added through the valve.

A second container was charged in exactly the same way except that a silica filled, silicone rubber reservoir ("Silescol TC 156/1" Esco, Ltd.) weighing 7.6 grams

was attached by wiring to the valve unit, and the added weight of propellant was 21.0 grams.

Both containers were stored for three weeks at room temperature, and their contents were then dispensed in a manner simulating normal usage. The container with the reservoir provided 1.78 liters of foam density within the range 80–100 grams per liter, whereas the container with no reservoir provided only 1.24 liters of foam in that density range.

These results are further shown in FIG. 3, wherein curve A shows the variation of foam density (coordinate y — gms., per liter) in relation to the amount of foam expelled (coordinate x — grams) when a reservoir is not employed, and curve B demonstrates this same relationship when a reservoir is used in accordance with the present invention. As can be seen, the incorporation of a reservoir maintains the density of the foam expressed substantially constant throughout use, the beneficial effect being particularly noticeable as the container approaches exhaustion with the density of the foam expressed by the container without the reservoir having risen rapidly at this terminal stage.

EXAMPLE 2

Example 1 was repeated, except that the container with no reservoir was charged with 6.0 grams of butane 40 propellant; and the reservoir was about a 2 mm. thick sheet of "CARIFLEX TR 1,101" thermoplastic rubber, (Shell Chemicals, Ltd.) of weight 10.0 grams, the container with reservoir being charged with 8.0 grams of butane 40 propellant. The container with no reservoir provided foam of density 70–134 grams per liter, whereas the container with the reservoir provided foam of density 78–104 grams per liter.

EXAMPLE 3

This example illustrates the application of the reservoir of the present invention in connection with a container dispensing a dry product.

A reservoir consisting of 12 grams of a propellant mixture, comprising 40 percent propellant 12 and 60 percent propellant 114 dissolved in a piece of "Silescol TC 156/1" silicone rubber, weighing 6 grams, was attached to a valve/dip tube assembly (formed as a bung with a hole in the middle and resting adjacent an enlarged portion on the dip tube which it could not slip past) which was in turn fixed into an 80 ml. can containing 12 grams of fine talc.

A similar can containing 12 grams of fine talc was not fitted with a reservoir but had 12 grams of the same propellant injected through the valve when the latter was in position. Thirty minutes after packing, the pressure in the can with the reservoir was 2.2 atmospheres and that in the can without the reservoir was 2.7 atmospheres.

Both cans were actuated normally until 7 grams of the contents had been expelled. Both were then actuated in an inverted position for 10 seconds after which period neither can was capable of dispensing powder at a useful rate because the can pressure had fallen almost to ambient pressure.

After standing for 20 minutes, the pressure in the first can had risen to 1.5 atmospheres and that in the second can to 1.2 atmospheres. Both cans were again actuated in an inverted position for 10 seconds; and, after standing for a further 20 minutes, the pressures had risen to 1.4 atmospheres and 0.3 atmospheres respectively. The

can containing no reservoir would not dispense appreciable further quantities of talc whereas that with the reservoir expelled almost all its remaining content of talc.

This example illustrates the manner in which a controlled release of propellant is achieved by the use of a reservoir, which will reduce the loss of propellant in the event of opening the valve when the can is inverted.

EXAMPLE 4

This example demonstrates the ability of unvulcanized natural rubber, prevulcanized natural rubber and mixtures thereof to form solutions with a hydrocarbon propellant.

Various mixtures of (1) a commercially available liquid unvulcanized rubber latex "Dunlop A 390" (Dunlop Chemical Products Division), having a solids content about 54 percent with a rubber body cast from the latex exhibiting a tensile load at break of 4.6 kg/cm² with 295 percent elongation, and (2) a commercially available liquid prevulcanized rubber latex "Dunlop A 330" (Dunlop Chemical Products Division), having a solids content about 61 percent with a rubber body cast from the latex showing a tensile load at break of 46.4 kg/cm² with 850 percent elongation were cast to form layers which were dried to form rubber sheets having a thickness of between 1 and 2 mm. About 10 g of each sheet were accurately weighed and placed in a glass aerosol bottle of 250 ml. capacity and a known volume (about 5 ml) of Butane 40 was added. The aerosol bottle was closed and the internal pressure was measured using a manometer.

As a solution formed between the rubber of the sheet and the Butane 40, the amount of liquid Butane 40 in the aerosol bottle, which was maintained at a temperature of about 23°C., decreased. Butane 40 was added to the aerosol bottle in known amounts to maintain a liquid propellant volume of about 5 ml. The amount of Butane 40 in the solution formed was measured with time.

The results shown in Table 2 were obtained after 50 hours:

Table 2

Test No.	Weight ratio of prevulcanized latex to unvulcanized latex used to form rubber sheet	Weight (g.) of Butane 40 in solution per 100 g. of rubber sheet
1	10:0	~74
2	9:1	108
3	8:2	88
4	7:3	117
5	6:4	102
6	5:5	115
7	4:6	129
8	3:7	113

As can be seen from Table 2, mixtures of prevulcanized and unvulcanized natural rubber can be produced which form solutions containing substantial amounts of propellant. Satisfactory physical properties for forming reservoirs can accordingly be obtained by using an appropriate weight ratio of prevulcanized to unvulcanized latex.

EXAMPLE 5

A similar series of experiments was effected using the method of Example 4 but with a mixture of Freons 12 and 114 (40:60 parts by weight respectively) as propellant instead of the Butane 40.

The volume of propellant initially added was about 10 ml and the amount remaining in the aerosol bottle was maintained at about this figure throughout the experiment.

Table 3 shows the results obtained after 120 hours:

Table 3

Test No.	Weight ratio of prevulcanized latex to unvulcanized latex used to form rubber sheet	Weight (g. $\pm$ approx. 20%) of a mixture of Freons 12 and 114 (40:60 parts by weight) in solution per 100 g. of rubber sheet
1	10:0	43
2	9:1	50
3	8:2	49
4	7:3	56
5	6:4	54
6	5:5	59
7	4:6	39
8	3:7	42

It can be seen from these results that rubbers derived from mixtures of unvulcanized natural rubber latexes and prevulcanized natural rubber latexes can form solutions containing more propellant than rubbers obtained from either the unvulcanized or the prevulcanized latexes alone.

EXAMPLE 6

Various commercially available unvulcanized and vulcanized synthetic rubbers were examined for their ability to form solutions with a variety of commercially available propellants.

Samples of each rubber weighing between 1 and 2 g. were accurately weighed and sealed in an aerosol container with about 10 g. of a particular propellant. The amount of propellant used and the size of the container were selected such that liquid propellant was present in the container throughout the experiment.

The sealed containers were stored at ambient temperature for a period of from 7 to 10 days and they were then opened, the rubber being weighed as soon as possible after opening of the container. The weight of propellant in solution could generally be measured to a reproducibility of about ± 5 percent.

Table 4 sets forth the results:

Table 4

Rubber	Propellant in solution g/100g of rubber				
	Butane 40	11	12	114	Freon 12+114 (40:60 by weight)
Butyl XX ⁽¹⁾	34	200	24	~30	32
I.S.R. Polybutadiene ⁽²⁾	82	n.m.	n.m.	n.m.	60
Vistanex L 140 ⁽³⁾	140(a)	(b)	78	20	43
Oppanol B 50 ⁽⁴⁾	130(b)	n.m.	n.m.	n.m.	~60
Oppanol B 100 ⁽⁵⁾	130(a)	(b)	80	19	45
Oppanol B 200 ⁽⁶⁾	100	n.m.	n.m.	n.m.	~45

n.m. = not measured; (a) = forms a gel; (b) = forms a liquid.

⁽¹⁾ A vulcanized isobutylene copolymer manufactured by Esco, Ltd. Tensile load at break, 44.8 kg/cm² with 850% elongation.

⁽²⁾ A polybutadiene manufactured by International Synthetic Rubber Co. Ltd., Southampton, England.

⁽³⁾ A polyisobutylene having an average molecular weight of 2,100,000 measured by the method of Flory P.J. (see Flory P.J.; principles of Polymer Chemistry, Cornell University Press, New York, 1953 and Flory P.J. and Fox T.G.; J. Amer. Chem. Soc. 73, (1951), (1904-1915) and an average molecular weight of from 117,000 to 135,000 by the method of Staudinger (see Ber., 63, (1930) 222 and ibid 63, (1930) 721). Manufactured by ESSO.

⁽⁴⁾ A polyisobutylene having an average molecular weight by the method of Schultz and Blaschke (see J. Prakt. Chem., 158, (1941), 130) of 380,000 measured as a solution in isooctane containing 0.2g./100 ml. The solution had a viscosity of 1.5×10^6 poise at 20°C and 8×10^6 poise at 100°C.

⁽⁵⁾ A polyisobutylene having an average molecular weight by the method of Schultz and Blaschke of 1,300,000 measured as a solution in isooctane containing 0.2g./100 ml. The solution had a viscosity of 3.6×10^{10} poise at 20°C and 6.7×10^8 poise at 100°C. Tensile breaking strength 2.2kg./cm² with 190% elongation.

⁽⁶⁾ A polyisobutylene having an average molecular weight by method of Schultz and Blaschke of 4,700,000 measured as a solution in isooctane containing 0.1g/100 ml. The solution had a viscosity of 1.5×10^{12} poise at 20°C and 10^{10} poise at 100°C.

(Oppanols B 50, B 100 and B 200 are manufactured by B.A.S.F., U.K., Ltd., London, England).

As can be seen from Table 4, the polyisobutylenes, Vistanex L 140 and Oppanol B 100 behave similarly with the various propellants used. Polyisobutylene rubbers can generally form solutions containing large amounts of propellants, but the higher molecular weight rubbers generally produce the mechanically stronger solutions and are therefore preferred for forming reservoirs for pressurized containers.

The vulcanized isobutylene-based copolymer Butyl XX was particularly good in forming satisfactory solutions with Freon 11 which formed liquids with the other rubbers tested.

EXAMPLE 7

This example demonstrates the rate at which specific suitable reservoir materials take up propellant in solution in a container.

The rubber samples used were:

"Dunlop A 330" prevulcanized latex rubber 5 mm. thickness.

"Cariflex TR 1101" thermoplastic rubber 2 mm. thickness.

"Oppanol B 100" polyisobutylene rubber 6 mm. thickness.

"Esco TC 156/1" silicone rubber 5 mm. thickness.

One sample of each rubber was immersed in liquid propellant, one was suspended in propellant vapor, a further sample was immersed in a shaving foam concentrate-propellant mixture and another wetted once by the concentrate and then suspended in the vapor phase over the concentrate.

The time necessary for each sample to take into solution 50% of the equilibrium amount of a butane propellant are set forth in Table 5:

Table 5

Rubber	In Liquid Butane	Over Liquid Butane	In Concentrate	Over Concentrate
Prevulcanized latex	1 hr.	8 hrs.	1 month	8 hrs.
Thermoplastic	½ hr.	5 hrs.	about 1 mth.	10 hrs.
Polyisobutylene	2 hrs.	15 hrs.	>>1 month	about 4 days
Silicone	1 hr.	15 hrs.	>1 month	about 7 days

The results indicated are not a strictly accurate simulation of commercial practice for the samples held in or above the concentrate, partly because of the need in practice to replace butane lost from the concentrate to the rubber samples; but the results do provide an indication of the amount of "aging" time needed between the packing of the container and use thereof to achieve the desired improvements in performance.

EXAMPLE 8

This example shows the effect on foam density of the use of a rubber reservoir holding propellant in solution in accordance with the present invention. Also, certain manufactured articles (e.g., bungs) were used to show that various rubbers, subjected to normal manufacturing processes, provided acceptable reservoir materials. The concentrate employed contained the following ingredients: stearic acid, 4.5 grams; lauric acid, 4.0 grams; triethanolamine, 3.5 grams; "PCL" liquid (emollient oil), 2.5 grams; "Sipon ESN" emulsifier, 1.5 grams and water to 100 grams.

The results are set forth in Table 6, wherein:

t20 — the approximate number of days from inserting the reservoir into the container to measuring the density of the foam dispensed, P20, (i.e., the aging period).

P20 — the density of the foam when 20 percent of the concentrate has been expelled in gms./liter (this represents the point at which the system has "settled down").

P90 — the foam density in gms./liter when 90 percent of the concentrate has been expelled.

F — the percentage determined by the following formula:

$F = 100 \times \frac{P90 - P20}{P90}$ for system with reservoir/
 $F = 100 \times \frac{P90 - P20}{P90}$ for system without reservoir but with same P20

Table 6

Reservoir	Concentrate Fill, gms.	Propellant	Prop. Fill gms.	t20	P20*	P90*	F
20 g Cariflex TR 1107 (3 mm. sheet)	100	12/114	20	9	65	70	17
20 g Cariflex TR 1107 (3 mm. sheet)	100	12/114	20	39	60	72	49
10 g Cariflex TR 1101 (~ 15 mm. cylinder)	100	butane	8	9	71	60	-26
10 g Cariflex TR 1101 (15 mm. cylinder)	100	butane	8	44	59	70	44
7.6 g Silicone Rubber bungs (10 mm. diameter cylinder)	100	butane	8	9	83	58	-25
7.6 g Silicone Rubber bungs (10 mm. diameter cylinder)	100	butane	8	44	60	58	-2
10 g Oppanol B200 (~ 8 mm. slab)	100	butane	8	9	96	60	-57
10 g Oppanol B200 (~ 8 mm. slab)	100	butane	8	44	71	69	-6
3.9 g Cariflex TR 1107 lining (~ 0.2 mm. thick)	150	12/114	14	29	108	122	21
3.8 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	18	28	80	91	32

Table 6—Continued

Reservoir	Concen- trate Fill. gms.	Propel- lant	Prop. Fill gms.	t20	P20*	P90*	F
7.6 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	21	28	79	94	45
15.4 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	25	28	85	102	35
10 g Cariflex TR 1101 (~ 15 mm. cylinder)	150	butane	10	9	62	77	58
20 g Cariflex TR 1101 (15 mm. cylinder)	150	butane	14	9	45	51	40
16 g Cariflex TR 1101 lining (~ 0.8 mm. thick)	100	butane	8	9	82	87	12
8 g Cariflex TR 1101 lining (~ 0.4 mm. thick)	100	butane	8	44	50	61	61
3.8 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	18	49	80	99	56
7.6 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	21	49	80	94	39
15.3 g Silicone Rubber bungs (10 mm. diameter cylinder)	150	12/114	25	49	88	106	42
10 g Cariflex TR 1101 (~ 15 mm. cylinder)	150	butane	8	49	80	98	41
20 g Cariflex TR 1101 (15 mm. cylinder)	150	butane	9	49	82	91	18

*Foam densities are uncorrected for buoyancy, true densities being approximately 1.2 gms./liter higher.

Ideally, the factor F should be zero; however, satisfactory performance is achieved when the increase in foam density is less than 40 percent of the increase occurring in the absence of a reservoir, viz., $F < 40$ per cent.

EXAMPLE 9

This example further illustrates the effect on foam

density of employment of a reservoir for supplemental propellant pursuant to the present invention. The concentrate used is identified in Example 8.

Various rubber materials were used as the reservoir with selected propellants, and the results are set forth in Table 7 (t20, P20, P90 and F being defined in Example 8):

Table 7

No. of Cans	Reservoir	Conc. Fill, gms.	Propellant	Propel- lant Fill, gms.	t20	P20	P90	F	% In- crease in avail. foam
3	10 g Cariflex TR 1101 (2 mm. sheet)	150	butane	8.0	46	83	95	26	0
2	5 g Cariflex TR 1101 on D/T (~ 1/2 mm. fluted cylinder with hole through middle)	150	butane	6.9	33	75	98	58	-1
3	10 g Esco RWH (~ 15 mm. diameter cylinder)	150	butane	8.0	46	75	94	49	0
3	10 g Dunlop A330 (2 mm. sheet)	150	butane	8.0	39	85	98	27	-1
3	5 g Dunlop A330 (2.5 mm. sheet)	150	butane	6.9	39	81	101	46	0
3	8.8 g Dunlop A330-Coating, 0.5 mm. thick	150	butane	7.7	33	90	112	40	-2
3	10 g Dunlop A390 (2 mm. sheet)	150	butane	8.0	39	83	97	30	-3
3	8.6 g Dunlop A390-Coating, 0.5 mm. thick	150	butane	7.7	33	90	111	39	-6
1	2.9 g Pre Vulcanized 'O' - ring 4 mm. thick	150	butane	6.4	33	80	102	51	-1
2	4 g Silicone tubing, 1 mm. thick	150	butane	8.0	33	64	84	69	-2
1	10 g Vistanex (8 mm. diameter rod)	150	butane	8.0	30	83	110	57	-4
2	10 g Rubber Foam	150	butane	8.0	33	66	78	41	-10
3	10 g Oppanol B15/capsule (liquid)	150	butane	8.0	33	88	97	18	-1
1	10 g Oppanol B15/capsule* (liquid)	150	butane	8.3	33	64	109	160	0
3	8 g Micro. Wax/capsule (solid flakes)	150	butane	7.7	33	76	82	16	+1
1	8 g Micro. Wax/capsule* (solid flakes)	150	butane	8.0	33	59	83	99	0
1	10 g Paraffin Wax/capsule (solid flakes)	150	butane	8.0	33	65	88	81	-2
3	10 g Silicone Bungs (10 mm. diameter cylinder)	150	12/114	21	55	93	100	14	0
3	5 g Silicone Bungs (10 mm. diameter cylinder)	150	12/114	17	55	95	103	15	0
3	6.8 g Silicone Bungs on D/T (5 mm. annuli)	150	12/114	18	33	107	103	-5	+1
3	2.5 g Silicone Tube on D/T (2 mm. thick)	150	12/114	15	33	105	114	13	+1
3	10 g Teat Rubber (1.5 mm. thick)	150	12/114	20	55	85	82	-8	-2
1	5.8 g Pre Vulcanized 'O' ring (4 mm. thick)	150	12/114	17	55	94	94	0	-1
3	7.9 g Dunlop A390-Coating (0.5 mm. thick)	150	12/114	19	33	76	96	63	-4
3	9 g Oppanol B200 (16 mm. diameter lump)	150	12/114	20	55	81	71	28	0
3	16.4 g Esco RWH (12 mm. diameter cylinder)	150	butane	10.8	33	87	79	—	—
	7.8 g Silicone Bungs (12 mm. diameter cylinder)	150	pre- dissolved 12/114 pre- dissolved	21.2	33	101	87	—	—

* Packed in Fischer-Porter bottles (but it is believed that propellant leaked during the experiment).

EXAMPLE 10

This example demonstrates the employment of a reservoir within a propellant-permeable capsule.

The capsule employed was a blow molded bag formed from a low density polyethylene film of 0.005 inch thickness. A butane propellant was utilized, and the reservoir materials forming a solution with the propellant were 10 grams of "Oppanol B 15" (B.A.S.F.), a very viscous liquid polyisobutylene having the following properties: a solution of 2.69 gms./100 ml. in tetralin at 20°C. having a viscosity at 20°C. of 5×10^6 poise and 3×10^4 poise at 100°C. (Ubbelohde viscometer); viscosity — average mol. wt. (Flory's method) — 95,000 and number average mol. wt. — 13,000) or 8 grams of a microcrystalline wax. The concentrate described in Example 8 was used.

The comparison of the foam density variation with and without a reservoir is shown in FIG. 4, wherein the x coordinate represents the amount of foam expelled in grams and the y coordinate, the foam density in gms./liter.

As can be seen from the figure, the density of the dispensed foam where no reservoir is used increases (Curves C and D). In contrast, employment of the polyisobutylene reservoir (Curve E) and the microcrystalline wax reservoir (Curve F) results in the maintenance of a substantially constant foam density.

EXAMPLE 11

This example demonstrates, for exemplary reservoirs in accordance with the present invention, the amount of propellant which is released as the vapor pressure within a system decreases.

A glass Fischer-porter bottle fitted with a standard aerosol valve and a capillary dip tube which terminated at the bottom of a test tube, and containing a manometer for measuring the internal pressure and a weight amount of a rubber reservoir, was used. The rubber reservoir comprised 7.1 grams of "Silecol TC 156" silicone rubber (properties of which have been described herein), formed in the shape of a cylindrical tubing which had been cut in half.

Propellant (the 40/60 weight percent mixture of 12/114) was introduced into the glass test tube to displace the air in the system and the bottle sealed. Further quantities of liquid propellant were added a little at a time through the valve and dip tube until the reservoir, which was only in contact with the vapor phase of the propellant, was saturated and the system was at equilibrium with an excess of liquid propellant in the test tube.

The excess liquid propellant was then led off and the pressure and weight of the total system (Fischer-porter bottle and contents) recorded. Further small amounts of propellant were bled off, and the system left to equilibrate. After each actuation or bleed off, the pressures and weights were again recorded. This was continued until the internal pressure within the system had fallen to about one atmosphere. The rubber was then removed, and it and the other components of the system weighed. The weight of the propellant still dissolved in the rubber reservoir at one atmosphere; and the weights of the propellant in the head space plus that in the rubber at various pressure, were obtained. By subtracting the weight of the head space vapor, obtained by a similar experiment without the reservoir, at the various pressures, the weight dissolved in the reservoir were obtained. All measurements were made at 23°C.

FIG. 5 is a graph of the data, the y-coordinate being the vapor pressure of the systems in atmospheres (Abs.) and the x-coordinate being the weight of propellant contained by the reservoir material in grams. As can be seen from this figure, when the vapor pressure decreases to 60 percent of its original value (viz., from 3.65 atmosphere Abs. to 2.19 atmospheres Abs., 11.5 grams of the propellant is released. This corresponds to about 74 percent of the propellant dissolved in the reservoir.

The same procedure was repeated with a rubber reservoir consisting of 9.4 grams of "Dunlop A 330" rubber. FIG. 6 is a graph showing the results. As can be seen, as the vapor pressure decreases to 60 percent of its original value, 4.2 grams of the 12/114 propellant are released. This corresponds to about 65 percent of the propellant dissolved in the reservoir.

The procedure was again repeated using 9.4 grams of the "Dunlop A 330" rubber, except using a "Butane 40" propellant. FIG. 7 is a graph similar to FIGS. 5 and 6, illustrating the weight of propellant which was contained by the reservoir material as the vapor pressure in the system decreased. Thus, as the vapor pressure drops to 60 percent of its original value, 7.5 grams of the "Butane 40" propellant are released. This corresponds to about 74 percent of the propellant which was originally in solution with the rubber reservoir.

Thus, as has been seen, the present invention provides a pressurized dispenser capable of improved performance by employing a reservoir allowing the use of propellants having higher inherent pressures and/or conferring a more uniform pressure during usage. The propellant is dissolved in solution with the reservoir and release is initiated as the head space in the dispenser increases when concentrate is expelled. In all types of pressurized dispenser systems, the present invention minimizes or at least reduces the deterioration of the dispenser functions and/or product properties following accidental discharge of part of the head space gases as compared with conventional pressurized dispensers. When the concentrate is dispensed as a foam, employment of a reservoir in accordance with this invention maintains the necessary propellant driving pressure for expelling the foam as well as maintaining the properties of the foam substantially the same throughout the dispenser life. It should be appreciated, however, that while the present invention may be employed to substantially maintain a propellant to concentrate ratio and to substantially maintain a uniform density of foam dispensed until virtually all of the concentrate or foam has been dispensed, commercial conditions may dictate that such ratio or foam density be maintained only until a substantial portion of the foam has been dispensed (e.g., about only 10 percent remaining). More specifically, use of the present invention typically produces a greater volume of foam from a given weight of concentrate with a foam density within a desired range. This also allows the satisfactory dispensing or expulsion of high density foam products (e.g., 300 gms./liter) such as toothpastes, which otherwise can suffer particularly extreme deterioration in mechanical properties of the foam during use.

With respect to the spraying of powder materials, the present invention allows the use of more powder per unit volume of the containers and provides a sprayed powder without any detectable chilling effect. Use with aqueous sprays increases the variety of formulations that may be used, for example, formulations which pre-

viously could not be employed due to the danger of propellant emulsifying in the concentrate.

In systems employing a mixture of propellants, use of the propellant reservoir of this invention can function as a vapor pressure depressant to provide an economical substitute for certain high cost propellants now used. Also, where a non-liquefiable propellant gas such as nitrogen is utilized for cost purposes, the performance of these systems suffers due to a considerable pressure drop during its life. The present invention allows use of a further supplemental propellant source to allow more uniform pressures to be realized.

The present invention also offers a means of dispensing a propellant gas free from liquid propellant, and it is also amenable to use with simple methods of propellant filling.

I claim:

1. A pressurized dispenser comprising a container provided with a valve-controlled outlet and containing a concentrate, and a reservoir holding propellant, positioned within the container, the reservoir comprising an organic substance with which the propellant forms a solution and over which the vapor pressure of the dissolved propellant is less than that of the pure propellant, the organic substance being capable of forming a solution with at least 15 percent of its own weight of propellant at room temperature, and the reservoir being capable of releasing propellant within the container as the contents of the container are dispensed.
2. A dispenser according to claim 1 wherein the reservoir is enclosed within a capsule pervious to propellant, said capsule confining therein a mobile solution of said substance and propellant.
3. A dispenser for discharging a product under pressure comprising a container having therein a reservoir for propellant, the reservoir being made of a solid organic polymeric substance which is capable of forming a solution with at least 15 percent of its own weight of propellant at room temperature, the vapor pressure of the dissolved propellant over the solution being thus reduced below that of pure propellant, and the reservoir being capable of releasing propellant within the container as the contents of the container are dispensed.
4. A dispenser according to claim 3 wherein the container contains a liquid mixture of a concentrate and propellant.
5. A dispenser according to claim 3 wherein the reservoir is a solid mass of the substance in which the propellant is dissolved and forms a part of a component of the dispenser.
6. A dispenser according to claim 3 wherein the reservoir is a solid mass of the substance in which the propellant is dissolved and is mounted on a component of the dispenser.
7. A dispenser according to claim 3 wherein the reservoir is a solid mass of the substance in which the propellant is dissolved and is coated on a component of the container.
8. A dispenser according to claim 3 wherein the substance is a polyisoprene.
9. A dispenser according to claim 3 wherein the substance is a polyurethane.
10. A dispenser according to claim 3 wherein the substance is an ethylene/vinyl acetate copolymer.

11. A dispenser according to claim 3 wherein the substance is a silicone rubber.

12. A dispenser according to claim 3 wherein the substance is a hydrocarbon rubber.

13. A dispenser according to claim 3 wherein the substance is a copolymer of isoprene and styrene.

14. A dispenser according to claim 3 wherein the substance is a copolymer of butadiene and styrene.

15. A pressurized dispenser component in the form of a valve and dip tube assembly for a container, said component having at least a part thereof made of a solid organic polymeric substance capable of forming a non-fluid solution with at least 15 percent of its own weight of propellant at room temperature when placed in a dispenser container in contact with propellant, said substance thereby forming a propellant reservoir over which the vapor pressure of the dissolved propellant is less than that of the pure propellant, said reservoir being capable of releasing propellant in response to a reduction in gaseous pressure within the container.

16. A method of manufacture of a valve-controlled pressurized dispenser which comprises introducing into a dispenser container a reservoir consisting of an organic substance, said substance being capable of forming a solution with at least 15 percent of its own weight of propellant at room temperature, the vapor pressure of the dissolved propellant over the solution being less than that of pure propellant, and the reservoir being capable of releasing dissolved propellant to reduce the fall in pressure in the head space of the container which would otherwise occur as the contents of the container are dispensed.

17. A method according to claim 16 wherein the reservoir is charged with propellant before introduction into the container.

18. A pressurized dispenser comprising a container having a valve-controlled outlet and containing a liquid concentrate and propellant mixture in a ratio to be dispensed, and a reservoir positioned within the container and comprising an organic substance holding propellant in solution with the vapor pressure over the dissolved propellant being less than that of the pure propellant, the reservoir being capable of releasing sufficient propellant to substantially maintain said liquid concentrate and propellant mixture ratio at least until a substantial portion of the concentrate has been dispensed.

19. A pressurized dispenser for foam comprising a container having a valve-controlled outlet and containing a concentrate and propellant mixture to be dispensed as a foam, and a reservoir positioned within the container and comprising an organic substance holding propellant in solution with the vapor pressure over the dissolved propellant being less than that of the pure propellant, the reservoir being capable of releasing sufficient propellant to maintain the density of the foam dispensed substantially uniform over the period until at least a substantial portion of the concentrate has been dispensed.

20. A pressurized dispenser employing a gaseous propellant to provide a predetermined driving pressure to dispense a concentrate which comprises a container having a valve-controlled outlet and containing a concentrate and gaseous propellant, and a reservoir positioned within the container and comprising an organic substance holding propellant in solution with the vapor pressure over the dissolved

23

propellant being less than that of the pure propellant, the reservoir being capable of releasing propellant to provide a supplemental source to substantially maintain the predetermined driving pressure.

21. A pressurized dispenser employing a gaseous propellant to provide a driving pressure to dispense a powder concentrate which comprises

a container having a valve-controlled outlet and containing a powder concentrate to be dispensed, and a reservoir positioned within the container and comprising an organic substance holding propellant in solution with the vapor pressure over the dissolved propellant being less than that of the pure propellant, the reservoir being capable of releasing more gaseous propellant than is present in a volume of the pressurized gaseous propellant equivalent to the volume occupied by the reservoir.

22. A method for assembling a pressurized dispenser for expelling a concentrate product, the dispenser including a container having a valve-controlled outlet and containing the concentrate product and a predetermined amount of a propellant, which comprises insert-

24

ing into the container a reservoir comprising an organic substance capable of holding propellant in solution with the vapor pressure over the dissolved propellant being less than that of the pure propellant, the reservoir being further capable of forming a solution with at least 15 percent of its own weight of propellant at room temperature, charging the container with the concentrate and propellant, the amount of the propellant being in excess of the predetermined amount, and allowing the reservoir to form a solution of at least a substantial portion of the excess propellant.

23. A pressurized dispenser for dispensing only a gaseous propellant comprising

a container having a valve-controlled outlet and a reservoir positioned within the container and comprising an organic substance holding propellant in solution with the vapor pressure over the dissolved propellant being less than that of the pure propellant, the reservoir being capable of releasing more gaseous propellant than is present in a volume of the pressurized gaseous propellant equivalent to the volume occupied by the reservoir.

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