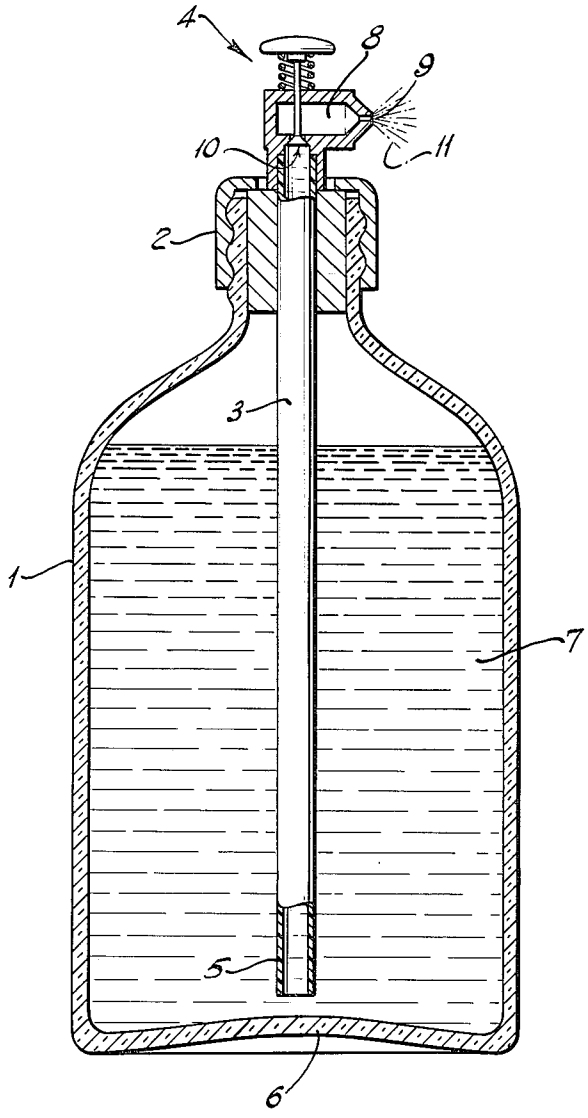
April 17, 1956 F. A. MINA ET AL 2,742,321

PACKAGES OF SELF-PROPELLING ATOMIZING LOW PRESSURE LIQUID COMPOSITIONS

Filed July 27, 1955



INVENTORS:
FRANCIS A. MINA
HENRY F. ANTCZAK
BY
Watson Johnson Leavenworth & Blair
ATTORNEYS.

United States Patent Office

2,742,321

Patented Apr. 17, 1956

2,742,321

PACKAGES OF SELF-PROPELLING ATOMIZING LOW PRESSURE LIQUID COMPOSITIONS

Francis A. Mina, Princeton, and Henry F. Antczak, Nixon, N. J., assignors to Chemway Corporation, a corporation of Delaware

Application July 27, 1955, Serial No. 524,781

9 Claims. (Cl. 299—95)

The present invention relates to packages of self-propelling low pressure liquid compositions, and to the nature of such liquid products contents thereof which permits delivery in effectively atomized form. More particularly, it relates to packages of such compositions which comprise a water-containing alcoholic liquid medium and a propellant dissolved in the medium, and dispensation of the compositions.

This application is a continuation-in-part of application Serial Number 427,688, filed May 5, 1954, now abandoned, which was a continuation-in-part of application Serial Number 360,688, filed June 10, 1953, now abandoned.

Previously it has been proposed to package in ampules a self-propelling liquid composition consisting of an organic liquid medium, a scent or odorous substance dissolved therein and methyl chloride propellant. However, such preparations have not proved to be satisfactory because of unpredictable and erratic variations in and excessiveness of pressures which prevent safely packaging in frangible containers of limited strength; insufficient fineness of spray particles when limited amounts of propellant were employed in an effort to improve the safety characteristics; flammability and toxicity. With limited amounts of methyl chloride propellant to reduce the pressures the liquid composition delivers from small orifices in streams several feet in length of either a continuous nature or as an in-line stream of coarse drops, rather than as an atomized mist. A degree of atomization of such liquid composition may be attained by increasing the methyl chloride to an amount constituting about half of the liquid composition but then the pressures become too high to permit safe packaging in frangible containers, such as glass bottles, and high percentages of propellant give to the atomized product an unduly high rate of evaporation which is unduly chilling to one's skin and is disagreeably uncomfortable. Also in large quantities the propellant may prove to be quite irritable and excessively toxic to the body tissues.

A general object of the present invention is to provide unique packages of liquid compositions of matter which permit unusually safe packaging of self-propelling water-containing alcoholic liquid compositions of the propellant-in-product type in frangible containers, the effective packaging thereof permitting when desired enhanced appearance of the containers and contents and desired atomized delivery of the latter; the preparation and packaging of such liquid products being economically practicable on a mass production basis involving automatic filling and closing machinery, the resulting packages assuring to the customers proper safety as to potential injury from container fragments and also when required as to flammability and toxicity of contents; the problems attendant upon prior art packaging, such as those discussed above, being efficiently solved or eliminated by the present invention.

A more specific object of the present invention is to

provide such propellant-in-product liquid compositions and to fill self-delivery containers therewith, the liquid compositions being characterized by a water-containing alcoholic liquid medium which may serve as a carrier and/or dispensable product, if desired a solute soluble in or miscible with the alcoholic liquid medium which may be a particular product to be dispensed or an additive to that constituted by the alcoholic medium, and a certain propellant selected from a specific group hereinafter particularized, the selected propellant being in solution in the alcoholic medium in certain definite proportions to assure unusually low internal pressures in the containers while permitting efficient self-propulsive delivery with effective atomization in the nature of a mist of fine particles or minute droplets.

Another object of the present invention is to permit safe packaging and marketing of liquid contents of the water-containing alcoholic type in frangible containers, such as glass bottles, while attaining, if desired, certain clarity and pleasing appearance of the liquid products in such containers when transparent, effectively free of "cloudiness" both of a permanent character, generally termed "milkiness," and of a transient character of the type wherein small globules of propellent liquid may float and swirl about in the body of liquid medium when the container is shaken, soon to collect and separate out into a defined separate strata, such as a pool, in the bottom of the container when the propellant is of greater specific gravity or as a stratum on the top of the liquid contents when the propellant is of lower specific gravity.

A further object of the present invention is to provide in such packages a water-containing alcoholic liquid medium or composition, which may be in the form of a cologne containing odor material, such as perfume emitting an agreeable odor, or in the form of other cosmetic preparation, or topical remedy, the liquid composition being of a self-propellent nature, confinable in relatively weak containers, such as glass bottles, under unusually low pressures which may be characterized by a brilliantly clear and sparkling appearance, the composition being, when desired, relatively non-flammable or at least not dangerously flammable, free of dangerous toxicity, and pleasant in feeling when applied to a person's skin.

An additional object of the present invention is to provide a "push button" package of self-propelling liquid composition, such as a cosmetic preparation, or equivalent preparation herein indicated, containing an alcoholic medium of saturated aliphatic monohydric alcohol containing not more than three carbon atoms and having a water content; a solute soluble in or miscible with the water-containing alcoholic medium which solute may be an agreeable aromatic substance; and a certain propellant selected from the group consisting of fluorinated, chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbons containing not more than two carbon atoms, butane, and mixtures thereof; in certain critical concentrations and proportions.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the apparatus or package embodying the features of construction, combination of elements and arrangements of parts, and the product contents thereof which possesses the characteristics, properties, and relation of components, all as exemplified in the detailed disclosure hereinafter set forth, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following

detailed description taken in connection with the accompanying drawing, in which:

The figure in the drawing is an elevational axial section of a package of the present invention, featured by a glass container fitted with a valved closure having a relatively small discharge orifice, and illustrating in diagrammatic form atomized delivery of liquid contents in the form of a fine mist when the closure valve is manipulated to permit self-propulsion of contents.

In the practice of the invention, there is produced a self-propelling liquid composition which comprises a "liquid medium," constituting a carrier medium and/or dispensable product, in the form of a water-containing solution of saturated aliphatic monohydric alcohol containing not more than three carbon atoms and having a concentration of at least about 75% by volume, and herein termed the "solvent" or "alcoholic constituent" of the liquid composition or preparation; if desired a substance to constitute a part of or the primary product to be dispensed, in solution in the alcoholic medium being herein termed "solute," i. e., it is a dispensable substance which is soluble in or miscible with the alcoholic medium or solvent; and a low boiling point "propellant" selected from the group consisting of fluorinated low molecular weight saturated aliphatic hydrocarbons containing not more than two carbon atoms, chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbons containing not more than two carbon atoms (such fluorinated, and chlorinated and fluorinated hydrocarbons being herein grouped together within the intended meaning of the terminology "fluorinated, chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbons containing not more than two carbon atoms"), butane, and mixtures thereof, in an amount by volume no greater than that which constitutes 50% of the entire liquid composition and preferably in a quantity which provides a substantially saturated solution of propellant in the water-containing alcoholic constituent or medium at normal room temperatures, e. g., about 70° F. In all cases the liquid compositions constituting the contents of the containers of the packages of the present invention are to contain a quantity of the propellant no greater than 50% by volume of the liquid composition, usually from about 10% to about 35% and preferably from about 15% to about 30% by volume of the composition since in most instances such amounts will provide the substantially saturated condition frequently essential to atomized mist delivery, and thus such liquid compositions may be characterized as being of the "propellant-in-product" type as distinguished from the "product-in-propellant" type where the propellant constitutes the major constituent of the liquid composition. It was unexpectedly found that the liquid composition contents of packages of the present invention which have been found to be of most practical and commercial value, embodying product ingredients of a preferred nature employ the propellants in amounts of about 10% to about 35% by volume of the whole composition in reaching a condition of substantial saturation. When a quantity of the composition of this propellant-in-product type is confined in a "see-through" or transparent container with the propellant being present in an amount appreciably greater than that required to attain substantial saturation at normal room temperatures of the water-containing alcoholic medium by the propellant, the excess of the latter gives to the package a source of hazard and also an unattractive appearance by collecting as a discernable pool of separated propellant in the bottom of the container or as large beads thereof moving about through the product medium when the package is shaken. If in a package in which the composition includes the alcoholic medium in the preferred or optimum alcohol concentration the quantity of the propellant present in the container is substantially below about 6% by volume less than that amount of propellant sufficient to attain exact saturation of the product medium by the propellant (i. e., the volume of the propellant is short of the ideal or optimum quantity for exact saturation at a specific normal room temperature by an amount greater than 6% of the optimum propellant quantity) the delivery from the package orifice will not be in the form of a desired misty spray in which the particles are of sufficient fineness, that is the fineness which is required for the demanded mist atomization, will not be produced. Moreover, larger amounts of such propellant undesirably reduce the alcoholic constituent or product medium content which can constitute a serious economical factor, and when an excess free pool of propellant is provided thereby likely will cause a hazardous condition in containers of shatterable material, such as glass, should the latter be employed, and in some instances such excessive amounts of propellant may cause development of undesirably higher pressures to increase the hazard; whereas lower amounts give an improper stream or in-line large droplet delivery. Thus when the quantity of the propellant present is between an amount which is about 6% less than the ideal or optimum amount for exact saturation at normal room temperature of the alcoholic medium of optimum alcohol concentration and an amount which may be slightly in excess of the ideal or optimum amount thus forming only a very small pool or stratum of separated propellant in the container, the product composition is here considered to be a substantially saturated solution which will assure the desired or demanded atomized mist delivery.

The optimum or preferred alcohol concentration by volume of the alcoholic medium of composition contents of these packages is about 95% for methanol, about 88% for ethanol, and about 80% for isopropanol and its equivalent propanol. Beyond such alcohol concentrations in the relatively small remainders of the ranges thereof up to the upper limits set by the various requirements as hereinafter fully explained the propellants may be employed in amounts less than those quantities required to give saturation of the alcoholic mediums appreciably greater than about 6%. As will be seen from the following tables such percentages by volume of propellants which may be employed to attain the desired results in such upper small remainders of the ranges will vary up to about 31% by volume. In other words, as one approaches the upper limit of the range of alcohol concentration for any particular alcoholic medium the quantity of the propellant which will provide acceptable mist deliveries may be below that for exact saturation of the alcoholic medium at these alcohol concentrations in progressively larger quantities but no less than 69% by volume of the quantity required for exact saturation. This appears to be due to the fact that as the alcohol concentration by volume is raised, i. e., the water content is reduced, increasingly greater quantities of the propellant are required to reach the point of exact saturation and in the upper portions of the ranges of alcohol concentration the quantity of propellant which will assure proper atomized mist delivery will have been added to the composition appreciably before the quantity necessary to exact saturation of the alcoholic medium has been incorporated. There is physically present in the composition a large enough quantity of propellant to assure atomized mist delivery of the alcoholic medium in such high alcohol concentrations even though the quantity of propellant present is appreciably below that amount which will go into solution in the alcoholic medium to attain saturation thereof. The following tables illustrate this feature of variation from exact saturation of the alcoholic medium by the propellant, the particular propellants selected being typical and those preferred for commercial practice of the invention. The following figures are given on the basis of one hundred (100) parts by volume of the liquid composition forming the contents of a container of a package of the present invention.

Table A

Alcohol concentration by volume of alcoholic medium	Parts by volume of $(CClF_2)_2$ (Freon 114) propellant to saturate alcoholic medium at 70° F.	Minimum parts by volume of the propellant to provide satisfactory spray pattern	Percentage difference of propellant below amount necessary for exact saturation at 70° F.
(I) Methanol:			
90%	14	13.6	2.85
95% (optimum)	27	25.5	5.55
96%	38	32.6	14.1
96.5%	50	34.5	31.00
(II) Ethanol:			
85%	17	16.5	2.94
88% (optimum)	24	23.2	3.33
90%	32	30.6	4.38
93%	50	35.4	29.20
(III) Isopropanol:			
75%	23	22.2	3.48
80% (optimum)	31	29.5	4.84
85%	50	36.0	28.00

Table B

Al. conc. by vol. of al. med.	Parts by vol. of prop. mix. [CCl_2F_2—10 parts by wt. ($CClF_2)_2$—90 parts by wt.] to sat. al. med. at 70° F.	Min. parts by vol. of prop. to give satisfactory spray pattern	Percent diff. of prop. below amount necessary for exact sat. at 70° F.
(I) Methanol:			
92% (optimum)	21.8	20.7	5.05
95%	39	30.5	21.8
96%	44.4	34.5	22.30
96.2%	50	36.2	27.60
(II) Ethanol:			
87% (optimum)	21.9	20.7	5.48
87.5%	23.5	21.9	6.81
88%	26.5	24.2	8.68
90%	33.5	30.5	8.96
92%	49	39.0	20.41
(III) Isopropanol:			
77% (optimum)	29.5	28.5	3.39
80%	39.2	34.6	11.73
85%	50	39	22.00

Further it has been found that the alcohol concentration of the water-containing alcoholic medium or constituent has a critical lower limit due to the fact that with alcohol concentrations appreciably less than 75% by volume, i. e., containing appreciably more than 25% water, the solubility of the particular propellant therein is reduced markedly so that the compositions have neither the desired appearance nor capability of forming an atomized spray, i. e., in which the particles are of sufficient misty fineness. An additional advantageous characteristic of the present liquid compositions is that only unusually low pressures are generated in the containers which are, at about 70° F., not in excess on 25 p. s. i. g., and usually in the range of about 11 to 15 p. s. i. g., which is of especial import when the compositions are packaged in relatively weak or frangible containers, such as glass bottles.

The water-containing alcoholic constituent of the liquid composition or dispensable preparation which is utilized in the practice of the present invention may be methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof; ethanol being particularly desirable. Further, it has been determined that the miscibility of the propellant in the alcohol is directly proportional to the number of carbon atoms of the alcohol, thus the miscibility increases from methanol containing one (1) through ethanol containing two (2) to isopropanol and its equivalent propanol containing three (3) carbon atoms, and also that the lower limit of alcohol concentration by volume for methanol is about 90%, for ethanol about 85%, and for isopropanol and its equivalent propanol about 75%. The present invention is concerned only with packages of self-propelling liquid compositions of the propellant-in-product type in which the product comprises or consists of an alcoholic constituent or medium having an appreciable water content and the propellant is one of those set forth herein. Thus, perhaps it would be just as well to speak of the water concentration of the water-containing alcoholic constituent or medium as of the alcohol concentration. In either view research has established that a critical point in the upper limit of alcohol concentration or lower limit of water concentration of these water-containing alcoholic mediums or solutions appears to be reached respectively between 96 and 97% by volume alcohol concentration the equivalent of which is between 3 and 4% by volume water concentration. With any of the mentioned saturated aliphatic monohydric alcohols containing not more than three carbon atoms when the alcohol concentration of the water-containing alcoholic medium is below 97% by volume, i. e., its water concentration is above 3% by volume, layering occurs in which propellant separates out of the alcoholic medium or product solution unless the relative proportions by volume of the propellant and product are adjusted so that the propellant is present in an amount no greater than that established amount which provides at normal room temperatures saturation of the water-containing alcoholic medium by the propellant. The appreciable water content in a concentration of more than 3% by volume but no greater than the herein indicated upper limit is the means whereby the employed amount of the specified propellants may be limited or reduced to effect an economy of use of the relatively expensive propellant ingredient while permitting attainment of desired atomized mist delivery. The greater the water content between the limits established by the present invention for these various alcohols, the lesser is the amount of the particular propellant selected from the specified group which will go into solution in the water-containing alcoholic medium. By using greater amounts of water within the limits herein established the amounts of the particular propellant ingredient selected from the recited group to attain substantial saturation of the water-containing alcoholic medium can be reduced. In using increased amounts of water for this purpose with suitable adjustments of the volumes of the selected propellant to avoid layering one must remember and fulfill the requirement that the volume of propellant is to be such as to satisfy the primary need for and demand of an acceptable delivery of the liquid produce in the form of an atomized mist or fine spray free from coarse drops and streaming. For example, with water-containing methanol alcoholic medium of an alcohol concentration of 96.5% by volume, i. e., a water concentration of 3.5% by volume, about 50% by volume of dichlorotetrafluoroethane propellant will go into solution therein and the alcoholic medium will be substantially saturated with the propellant to give an atomized mist delivery at normal room temperature. If the alcohol concentration of the water-containing methanol is reduced to 96% by volume by use of 4% by volume of water about 38% by volume of the dichlorotetrafluoroethane propellant will go into solution therein to give a good spray pattern of atomized mist under like conditions. In substituting water-containing ethanol for the methanol alcoholic medium it has been found that as much as 50% by volume of dichlorotetrafluoroethane propellant would go into solution in the water-containing ethanol medium having an alcohol concentration of about 93% by volume, i. e., a water concentration of about 7% by volume, to attain saturation of the alcoholic medium which it has been observed assures the atomized mist delivery at normal room temperature that was desired. Satisfactory atomized mist spray patterns under like conditions are attained at alcohol concentrations of the water-containing ethanol medium of 94% and 95% by volume as well as at the 93% by volume alcohol concentration, but values of the latter above 95% by volume result in unsatisfactory spraying of the propellant-in-product composition in the form of a central stream flanked by coarse drops with the central stream breaking up into coarse drops at a distance of

about six feet (6') from the outlet orifice of the package spray head. When isopropanol or its equivalent propanol was substituted for the methanol or the ethanol it was found that as much as 50% by volume of the dichlorotetrafluoroethane propellant would go into solution in the water-containing isopropanol or propanol medium having an alcohol concentration of about 85% by volume, i. e., a water concentration of about 15% by volume, saturation of the alcoholic medium by the propellant being attained at that point and assuring the desired atomized mist delivery. Good spray patterns under like conditions are attained at alcohol concentrations by volume of the water-containing isopropanol and propanol mediums of 86%, 87% and 88% in addition to that at the 85% by volume alcohol concentration, but isopropanol and propanol alcohol concentrations above 88% by volume cause the propellant-in-product composition to be delivered from the package spray head orifice in the form of a coarse drops-flanked stream about six feet (6') long which breaks up at that distance into coarse drops. The lower limits of the ranges of the concentrations by volume of the four alcohols to be used in the practice of the present invention are dictated chiefly by the spray patterns. At alcohol concentrations below about 75% by volume of isopropanol and propanol, below about 85% by volume of ethanol and below about 90% by volume of methanol when the water-containing alcoholic mediums are saturated with the selected propellants the deliveries of the compositions from the packages are weak sprays of coarse drops since there is insufficient propellant in solution to explode the released compositions into strong sprays of atomized mist.

When a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane, such as 10 parts by weight of CCl_2F_2 (Freon 12) and 90 parts by weight of $(CClF_2)_2$ (Freon 114), is substituted as the propellant for the dichlorotetrafluoroethane a somewhat similar pattern of alcohol concentrations to give a proper atomized mist delivery is experienced. In the event that water containing methanol is employed as the water-containing alcoholic medium an alcohol concentration of about 96.2% by volume will take into solution about 50% by volume of the propellant mixture and a good spray pattern results at 70° F. When water-containing ethanol is employed an alcohol concentration thereof of about 92% by volume will take up about 49% by volume of the propellent mixture to give a good spray pattern at 70° F. In the use of isopropanol and its equivalent propanol water-containing solutions thereof will at alcohol concentrations of about 85% by volume take up about 50% by volume of the propellent mixture to give an excellent atomized mist delivery at 70° F. In the employment of mixtures of any two or three of these alcohols as the solvent or alcoholic constituent the concentration by volume of each component alcohol will follow the pattern dictated by the requirement of about 75% and upward to just less than 97% of isopropanol and its equivalent propanol, about 85% and upward to just less than 97% of ethanol and about 90% and upward to just less than 97% of methanol so that the concentration by volume of the alcoholic mixture will be of the order of that pattern. For example, if a mixture of isopropanol (or its equivalent propanol) and ethanol be employed as the alcoholic constituent in the proportions of about equal parts, the minimum concentration by volume of the mixture will be about 80%.

It will thus be understood that in the production of packages of the present invention the alcohol concentration of the water-containing alcoholic medium is to be kept within certain limits to assure the attainment of the desired characteristics including the required atomized mist delivery in the form of a very fine strong spray of good pattern. The use of methanol for the water-containing alcoholic medium dictates a range of alcohol concentration of from about 90% to about 96.5% by volume, i. e., the water concentration will be in the range of about 3.5% to about 10% by volume. If ethanol be employed in the preparation of the water-containing alcoholic constituent the alcohol concentration thereof should be kept within the range of about 85% to about 95% by volume, i. e., the water concentration will be maintained in the range of about 5% to about 15% by volume. When isopropanol or its equivalent propanol is used in making up the water-containing alcoholic medium the alcohol concentration thereof should be within the range of about 75% to about 88% by volume, i. e., the water concentration should be within the range of about 12% to about 25% by volume.

The solute which is to be dispensed should be soluble in or miscible with the water-containing alcoholic medium in an effective amount and may be a deodorizer, as dimethylphthalate and pine oil; a medicinal substance as benzoin, an anti-histamine, novocaine, procaine and ethyl para-amino benzoate; a lacquer substance, as shellac, ester gum and synthetic resins soluble in the alcohol medium; an antiperspirant; tannic acid; umbelliferone; or an insecticide as rotenone, rotenoids and dichloro-diphenyl-trichloroethane; of an odorous substance or material emitting an agreeable or pleasant odor, and commonly termed a "perfume." The perfume ingredient may be either solid or liquid and either of natural or synthetic origin. Thus, the perfume ingredient may be an essence of various flowers, as the rose, lavender, gardenia, carnation, lilac and lily-of-the-valley; and irone and other synthetic odorous substances, for example, geranyl acetate, eugenyl acetate, phenyl alkyl ethers, as phenyl ethyl ether and esters as methyl salicylate; and such perfume ingredient may be one or a mixture of a plurality of such essences in the form of essential oils.

The propulsion of the liquid composition to be atomized is chiefly effected by means of the presence therein of the particular propellant, e. g., from about 10% to about 35% of one or more of the recited propellent materials, the boiling point of the propellant being at normal atmospheric pressure lower than normal room temperatures, such as less than about 70° F. at one atmosphere. It will be realized that the propellant may be either a single one of the recited propellent compounds or a compatible admixture of such compounds if the mixture has such a boiling point, and further that the propellant shall be soluble in the alcoholic preparation to be atomized.

The particular fluorinated, and chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbon propellent compounds may be represented generally by the formula $C_nH_xCl_yF_z$, wherein n is a whole number (usually 1 or 2), x is zero or a whole number, y is zero or a whole number, and z is a whole number, and the sum of x, y and z is equal to $2n+2$. More particularly, mention may be made of the following:

monochlorotrifluoromethane, trichloromonofluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, difluoroethane, and difluoromonochloroethane. The use of dichlorotetrafluoroethane has led to markedly satisfactory results.

Some of the herein recited propellent compounds, such as trichloromonofluoromethane and trichlorotrifluoroethane, boil at temperatures higher than 70° F. at a pressure of one atmosphere and thus, alone, are not practical for propellants in the practice of the present invention in climates where normal room temperatures, at which the preparations are to be mist delivered, are below their boiling points. However, they are useful in propellent mixtures of the present invention, being utilized as pressure diluents for those propellent compounds herein recited which have the lower boiling points and thus the higher pressures. For example, the present invention has been successfully practiced by mixing dichlorodifluoromethane with dichlorotetrafluoroethane in such proportions as to form

propellent mixtures having vapor pressures below the maximum limit of near 25 p. s. i. g. under like conditions. In packages of the present invention butane acts very similar to dichlorotetrafluoroethane wherever the greater flammability of the former is of no importance or is blanketed to an acceptable degree by the other ingredients.

When such a liquid composition or preparation, comprising the water-containing alcoholic constituent or solvent, the solute and the particular propellant, is confined in indicated proportions in a closed container, such as that indicated at **1** in the drawing, an internal pressure of relatively low order is created therein. Such internal pressure is of the order of about 11 to 15 p. s. i. g. at about 70° F. when the proportions of the ingredients of the liquid composition are of the order herein taught. That is an important safety factor particularly when frangible containers, such as glass, are employed as indicated in the drawing. Appearance and economy dictate the desirability of using for packaging many products in transparent containers, such as those formed of clear glass and certain "see-through" synthetic plastics, e. g., polystyrene and the like, but a tendency for some such materials to shatter when subjected to blows, such as when dropped, with attendant hazard of jagged pieces and slivers thereof to fly about under the driving force of the internal pressure, demand that the latter be kept below a safe maximum, and preferably in the range of about 11 to 15 p. s. i. g. at normal room temperatures. Safe pressures may be somewhat higher, such as up to about 20 to 25 p. s. i. g., particularly where stronger or suitably protected containers are employed; and lower pressures, e. g., 10 p. s. i. g., may be suitable for proper propulsive delivery of the products in atomized form when certain types of ingredients are used in certain proportions within the scope of the present invention.

Reducing the amount of propellant by increasing the water content of the alcoholic medium within the specified limits while limiting the propellant to that quantity which will go into solution in the water-containing alcoholic medium under particular conditions and at normal room temperature does not materially alter the internal pressure of the package. Increased amounts of water with attendant decrease in the amount of propellant through the entire specified range for the particular water-containing alcohol being used will at most cause a decrease in the internal pressure within the package of only a few p. s. i. The maximum internal pressure is that of a confined body of the selected propellant alone and that of any particular package of the present invention wherein the propellant is in solution in the water-containing alcoholic medium is from a few p. s. i. below that maximum up near and closely approaching the latter. I. C. C. regulations permit such packaging and distribution in frangible and relatively weak containers, such as glass bottles, when their internal pressures are no greater than or are kept below 25 p. s. i. g. at 70° F. This dictates that the maximum internal pressures of the packages of the present invention no greater than 25 p. s. i. g. which in turn dictates in part the selection of the propellant. No low boiling point liquid can serve as a propellant in a package of the present invention if the packaged composition containing it can develop when confined under normal conditions a pressure in excess of 25 p. s. i. g. at 70° F. It is thus best to select such propellants for use with this invention as have vapor pressures no greater than 25 p. s. i. g. at 70° F. and other requirements of the present invention dictate its selection from the specified group consisting of flourinated, chlorinated and flourinated low molecular weight saturated aliphatic hydrocarbons containing not more than two carbon atoms; butane; and mixtures thereof.

The present invention is concerned chiefly with factors of appearance of the products when packaged in transparent or "see-through" containers, safety when the containers are of frangible and potentially dangerous shatterable character, and particularly efficient delivery in atomized form in the nature of a cloud or mist of very fine particles or minute droplets; and not with any particular improvements in designs of delivery apparatus. For example, the glass bottle **1** illustrated in the drawing is equipped with conventional delivery equipment in the form of anchoring cap means **2** which holds in position mounting means for an eduction or dip tube or stand pipe **3** serving as a gas-tight closure for the bottle and a discharge valve and nozzle assembly **4** shown communicating with the duct provided by the tube. The valve and nozzle assembly **4** is illustrated not by way of dictating any particular delivery apparatus since many conventional types have been found to be suitable.

As is well understood in this art and as shown, the bottom end **5** of the eduction tube **3** extends to near the bottom **6** of the container **1** to assure a delivery of a maximum amount of the body **7** of contained liquid composition, the latter, however, being unique as to ingredients and proportions thereof in accordance with the present invention. The discharge passage leading from the container **1** includes the duct provided by the eduction tube **3** and a passage portion **8** of no particular design extending through the nozzle assembly **4** to a relatively small discharge orifice **9**, with a biased valve **10** controlling flow through the nozzle passage portion. Conventional spray heads for such types of packages have outlet or discharge orifices of the order of 0.018" to 0.019" in diameter (which may vary from about 0.015" to 0.020" in dia.); and conventional aerosol practices allow orifices thereof to be of a size within the range of about 0.005" to 0.025" in diameter depending upon the viscosity of the product to be dispensed and other characteristics of the packages. The discharge passage may be of substantially uniform cross-section throughout up to the discharge orifice, and experience has taught that with certain compositions of the present invention, such a simplified uniform discharge passage may give improved atomization.

When the valve **10**, normally biased to closed position, is opened, such as by manual manipulation or finger depression, the internal pressure in the container **1**, due to the vapor pressure of the particular low boiling point propellant in solution in the water-containing alcoholic medium or solvent, and possibly due to some extent to that of the alcohol of the latter in gaseous phase with the propellent vapors in the gas head above the body of liquid **7**, forces the liquid composition out through the discharge passage past the valve **10** to be delivered as an atomized spray or mist from orifice **9**, as diagrammatically indicated at **11**, and not as a long stream of substantially continuous form or substantially in-line large drops. This desired atomization is effected without the employment of excessive and unsightly separated amounts or pools of contained propellant and without the employment of dangerously high internal pressures of the order of 40 p. s. i. g. at normal room temperatures of about 70° F.

The packaged product presents an attractive, sparklingly bright and clear appearance through the transparent or "see-through" container, and in order to assure maintenance of such desirable esthetic characteristics, the propellent ingredient of the composition preferably may be employed in an amount near but slightly less than the ideal or optimum amount required for complete or exact saturation of the solute-containing alcoholic medium by the propellant, and within the ranges of variations indicated above. Thus, at normal room temperatures of the order of about 70° to 90° F. clarity is attained; and even at somewhat reduced temperatures, such as down to about 65° F., there is little tendency for some of the propellant in solution in the water-containing alcoholic medium to separate out of the composition. By incorporating such amounts of the specified propellent ingredient an internal pressure of safe order, which will give the desired

atomized delivery, is assured. Of course, at elevated temperatures up to about 130° F., the standard test maximum, the clarity in appearance and the atomized delivery are maintained since the amounts of propellant soluble in the solute-containing medium to saturation increases with temperature, and the atomizing characteristics are progressively enhanced. The propellants here proposed assure another important safety factor. The pressure-temperature relationship curves curve down away from oblique straight lines to progressively greater degrees approaching the horizontal with progressive increases in temperature. This is markedly characteristic of dichlorotetrafluoroethane (Freon 114) which due to the nonflammability thereof and freedom from tendency to irritate human skin is particularly desirable for use in practicing certain phases of the present invention.

If the liquid contents of a package of the present invention were in the nature of a product-in-propellant composition, or the liquid composition was confined in the container with a pool of free excess propellant separated from the product medium sudden release of the contents from confinement, such as may attend breakage of the container, would be accompanied by prompt and vigorous boiling of the liquid propellant to vapor phase, thus rapidly converting potential energy to kinetic energy with a minimal lag. If the liquid composition is of the type herein taught, i. e. propellant-in-product where the product medium constitutes at least half by volume of the composition or the major constituent in which the propellant is dissolved, and there is no appreciable amount of propellant collected as free excess in a separate pool or stratum, sudden release from confinement by the container results in only slow retarded boiling to vapor phase with checked transition from potential force to kinetic force through an appreciable lag phase. If the container be of shatterable material, such as glass, and the liquid contents be of the latter type of propellant-in-product with no appreciable excess pool of propellant, fragments of the broken container will be propelled with minimum danger only by the force of the internal pressure caused by the vapor phase propellant in the gas head; and by the time the propellant slowly boils out of the product medium or water-containing alcoholic constituent the force of the gas head pressure propulsion of fragments will be spent and slow boiling of propellant dissolved in the product medium with attendant slow change of potential force to kinetic energy will be harmless and incapable of dangerously supplementing the gas head drive of fragments.

As an illustrative embodiment of a manner in which the invention may be practiced, the following examples are presented. The parts are by volume.

Example I

Ethanol (87% alcohol concentration) ---------- 75 parts by volume.
Dichlorotetrafluoroethane--- 25 parts by volume.
Perfume---------- Q. s. ("sufficient quantity").
Package in a valved container having a dip tube.

Example II

A composition suitable for the deodorization of air may be prepared in the following manner: Mix 1 gm. of perfume oil and 0.5 gm. of diethyl phthalate into 85 ml. of isopropanol and add water q. s. to 100 ml. to form an alcoholic medium. To 52 ml. of this alcoholic medium in a closed valved container having a dip tube add 48 ml. of dichlorotetrafluoroethane to form a pressurized package.

Example III

A composition may be prepared containing 98 ml. of ethanol of an alcohol concentration of 95%, 2 gms. of ethyl p-amino benzoate, perfume q. s., and water q. s. to 100 ml. To this water-containing alcoholic medium may be added dichlorotetrafluoroethane in the relative proportion of 30 parts to 70 parts by volume within a valved container having a dip tube.

Example IV

Another cosmetic preparation may be packaged as a variation of Example I by utilizing as the propellant 12.5 parts by volume of dichlorotetrafluoroethane and 12.5 parts by volume of butane, with which is mixed 75 parts by volume of ethanol of an alcohol concentration of about 87% and perfume q. s. which may be a fraction of 1% to a few per cent. Also butane may be substituted wholly for the dichlorotetrafluoroethane of Example I.

Example V

There may be substituted for the propellant ingredient of any of the above examples a propellant admixture of dichlorotetrafluoroethane, dichlorodifluoromethane and trichlorotrifluoroethane in the relative proportions by weight, respectively, of about 23%, about 15.5% and about 61.5%, and in the quantities by volume indicated in these examples. Such an admixture propellant has a pressure of about 17 p. s. i. g. at about 70° F.

Example VI

An antiseptic aerosol tincture may be packaged by adding to 92 ml. of ethanol 0.2 gm. benzalkonium chloride and water q. s. to 100 ml. to form an alcoholic medium. 52 ml. of the alcoholic medium is housed with 48 ml. of (Freon 114) dichlorotetrafluoroethane in a valved container having a dip tube. 48 ml. of 10 parts by weight of Freon 12 and 90 parts by weight of Freon 114 may be substituted for the Freon 114.

Example VII

To 92.3 ml. of ethanol add 2 gms. perfume oil and water q. s. to 100 ml. House 52% by volume thereof with 48% by volume of dichlorotetrafluoroethane in a valved container having a dip tube.

The present invention is particularly important to the production, marketing and use of cosmetic preparations, such as colognes, deodorizers, and antiperspirants, as well as tinctures, etc. For example, it has been found to be highly advantageous to the marketing of self-propulsive colognes in attractive, "push button" or valved glass bottles having eduction or dip tubes. "Example I" above is well suited to the latter purpose and the "q. s." (quantity sufficient) amount of the concentrated perfume essence may be of the order of about 2% by weight of perfume-containing alcoholic medium; a fraction of one percent, e. g., about 0.5% being suitable when highly odorous material is employed as the perfume ingredient; but of course when desired greater quantities, e. g., up to about 8% by weight of perfume oil, may be employed.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the constructions or packages set forth and the contents of the containers thereof without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A package of relatively low pressure, self-propelling

liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of saturated aliphatic monohydric alcohol selected from the group consisting of methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof, having a water concentration greater than 3% by volume, the alcohol concentration of said alcoholic medium being by volume from about 75% to about 88% for isopropanol and its equivalent propanol, from about 85% to about 95% for ethanol and from about 90% to about 96.5% for methanol; said propellant being selected from those of the group consisting of fluorinated low molecular weight saturated aliphatic hydrocarbons having a carbon content of C_1–C_2, chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbons having a carbon content of C_1–C_2, normal butane, and mixtures thereof, which have a boiling point at one atmosphere lower than normal room temperatures and a vapor pressure up to 25 p. s. i. g. at 70° F.; said propellant being present in said liquid composition in an amount up to 50% by volume thereof and from about 69% by volume of that quantity which provides a saturated solution of the alcoholic medium at normal room temperatures to that quantity which provides such saturation, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

2. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of saturated aliphatic monohydric alcohol selected from the group consisting of methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof, having a water concentration greater than 3% by volume, the alcohol concentration of said alcoholic medium being by volume from about 75% to about 88% for isopropanol and its equivalent propanol, from about 85% to about 95% for ethanol and from about 90% to about 96.5% for methanol; said propellant being selected from those of the group consisting of fluorinated low molecular weight saturated aliphatic hydrocarbons having a carbon content of C_1–C_2, chlorinated and fluorinated low molecular weight saturated aliphatic hydrocarbons having a carbon content of C_1–C_2, normal butane, and mixtures thereof, which have a boiling point at one atmosphere lower than normal room temperatures and a vapor pressure up to 25 p. s. i. g. at 70° F.; said propellant being present in said alcoholic medium in an amount constituting from about 10% to about 35% by volume of the liquid composition with the amount of propellant in solution being from about 23% less than and up to about that quantity which provides at normal room temperature a saturated solution thereof in the alcoholic medium, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

3. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of saturated aliphatic monohydric alcohol selected from the group consisting of methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof, having a water concentration greater than 3% by volume, the alcohol concentration of said alcoholic medium being by volume from about 75% to about 88% for isopropanol and its equivalent propanol, from about 85% to about 95% for ethanol and from about 90% to about 96.5% for methanol; said propellant being dichlorotetrafluoroethane present in said liquid composition in an amount up to 50% by volume thereof and from about 69% by volume of that quantity which provides a saturated solution of the alcoholic medium at normal room temperatures to that quantity which provides such saturation, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

4. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of saturated aliphatic monohydric alcohol selected from the group consisting of methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof, having a water concentration greater than 3% by volume, the alcohol concentra-

tion of said alcoholic medium being by volume from about 75% to about 88% for isopropanol and its equivalent propanol, from about 85% to about 95% for ethanol and from about 90% to about 96.5% for methanol; said propellant being dichlorotetrafluoroethane present in said liquid composition an amount up to 50% by volume thereof and from about 6% less than and up to about that quantity which provides at normal room temperature a saturated solution of dichlorotetrafluoroethane in the alcoholic medium, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

5. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of ethanol having an alcohol concentration from about 85% to about 95% by volume; said propellant being dichlorotetrafluoroethane present in said ethanol alcoholic medium in an amount constituting from about 16.5% to about 35.5% by volume of the water-containing ethanol and dichlorotetrafluoroethane content, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

6. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution consisting of a water-containing alcoholic solvent of ethanol having an alcohol concentration of about 88% by volume, and an alcohol-soluble solute of a perfume ingredient in solution in said solvent in an effective amount and up to about 8% by weight of the dispensable product solution; said propellant being dichlorotetrafluoroethane present in said liquid composition in an amount from about 23% to about 24% by volume of the solvent and dichlorotetrafluoroethane content.

7. A package of self-propelling propellant-in-product liquid composition comprising, in combination, a hermetically sealed glass container having a valved outlet terminating in a relatively small discharge orifice and an eduction tube leading to the valved outlet from a point near the bottom of said container, and a body of liquid composition consisting essentially of water-containing ethanol solvent having an alcohol concentration of about 85% to about 95% by volume, a dispensable product alcohol-soluble solute in solution in the solvent, and a propellant of dichlorotetrafluoroethane in an amount constituting from about 16.5% to about 35.5% by volume of the solvent and dichlorotetrafluoroethane content; said dichlorotetrafluorethane propellant being in solution in said solute-containing solvent in an amount from about 6% less than and up to about that quantity which provides at normal room temperature a saturated solution of dichlorotetrafluoroethane in said solvent, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures; said body of liquid composition being confined in said container under the vapor pressure of the propellant which at normal room temperatures is about 11 p. s. i. g. to about 15 p. s. i. g.

8. A package of relatively low pressure, self-propelling liquid composition comprising, in combination, a fluid-tight container of limited strength; means providing a relatively small discharge orifice for atomized dispensation of contents and an openable closed passage leading to said discharge orifice from the interior of said container at a point near the bottom thereof; and a contained two-phase fluid system confined in said container at a pressure of from about 11 p. s. i. g. to about 15 p. s. i. g. at normal room temperatures, said system consisting of a body of propellant-in-product liquid composition having a water-containing alcoholic constituent as a solvent, a dispensable product alcohol-soluble solute in solution in the solvent and a propellant in solution in the solute-containing solvent, and a gas head comprising some of the propellant and solvent in vapor phase; the solvent being ethanol having an alcohol concentration from about 85% to about 95% by volume; said propellant being dichlorotetrafluoroethane with the amount thereof in said container constituting from about 16.5% to about 35.5% by volume of the solvent and dichlorotetrafluorethane content and from about 6% less than and up to about that quantity which provides at normal room temperature a saturated solution of dichlorotetrafluoroethane in said solvent, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

9. A package of relatively low pressure, self-propelling liquid composition comprising a fluid-tight container having closure means providing a small discharge orifice for atomized dispensation of contents and a valve-controlled passage leading to said discharge orifice from the interior of said container at a point of immersion in the liquid composition, said container confining therein a body of liquid composition for delivery through the orifice in liquid phase consisting essentially of a liquid mixture of dispensable product solution and volatile propellant and being of the propellant-in-product type which immediately upon orifice delivery will be converted to an atomized mist by change of the contained propellant from liquid to gaseous phase, the body of liquid composition being confined in the container under a vapor pressure of the propellant up to 25 p. s. i. g. at 70° F.; said dispensable product solution being chiefly a water-containing alcoholic medium of saturated aliphatic monohydric alcohol selected from the group consisting of methanol, ethanol, isopropanol and its equivalent propanol, and mixtures thereof, having a water concentration greater than 3% by volume, the alcohol concentration of said alcoholic medium being by volume from about 75% to about 88% for isopropanol and its equivalent propanol, from about 85% to about 95% for

ethanol and from about 90% to about 96.5% for methanol; said propellant being a mixture of dichlorodifluoromethane and dichlorotetrafluoroethane with the latter being present therein in such predominant amount that the propellant mixture has a boiling point at one atmosphere lower than normal room temperatures and a vapor pressure up to 25 p. s. i. g. at 70° F., said propellent mixture being present in said liquid composition in an amount up to 50% by volume thereof and from about 72% by volume of that quantity which provides a saturated solution of the alcoholic medium at normal room temperatures to that quantity which provides such saturation, the amount of said propellant in solution in said alcoholic medium being at least that quantity which provides at the selected alcohol concentration of said medium atomized mist delivery of the dispensable product solution at normal room temperatures.

References Cited in the file of this patent

UNITED STATES PATENTS

1,892,750	Rotheim	Jan. 3, 1933
2,621,014	Efford	Dec. 9, 1952

FOREIGN PATENTS

557,259	Germany	Aug. 20, 1932

OTHER REFERENCES

Moore: American Perfumer and Essential Oil Review, October 1950, pp. 293 to 296.

Du Pont Technical Bulletin, volume 7, June 1951, pp. 8, 84, 85.

Handbook of Chemistry and Physics, Thirty-first edition (1949), pp. 1922, 1924.