

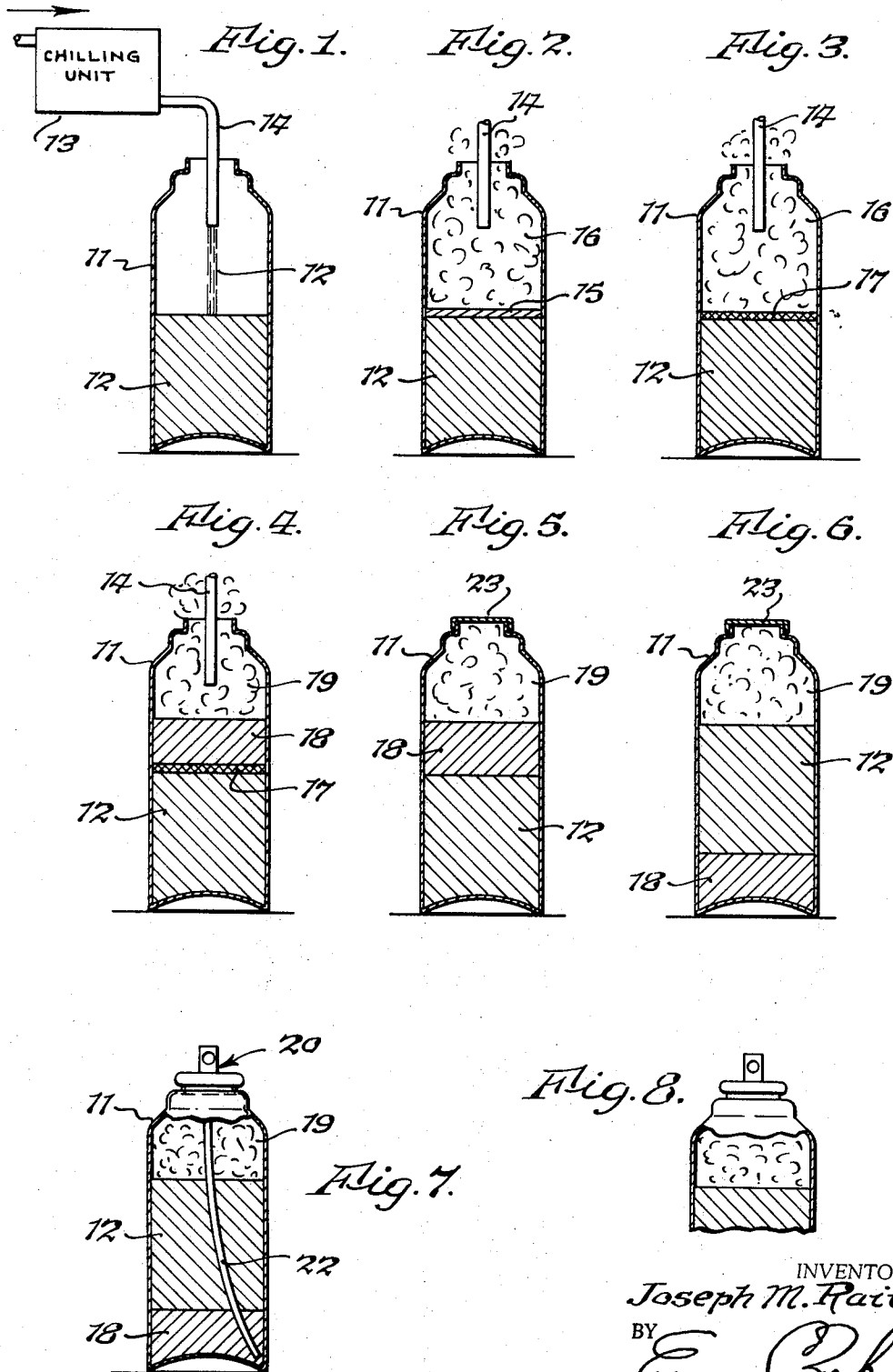
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METHOD OF FILLING AEROSOL CONTAINERS AND THE LIKE

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METHOD OF FILLING AEROSOL CONTAINERS AND THE LIKE

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This invention is concerned with a method of adding moderately low boiling liquids to partially filled containers.

More specifically, the invention of the present instant provides a method for filling containers which prevents the undue loss of a low-boiling component by interposing a temporary anti-mixing barrier within the container.

The filling of containers with mixtures of various liquids represents an important aspect of the production of many products. This is particularly true for example, in the case of the dynamic ever-growing aerosol industry. As in other important segments of industry there are certain problems which not only operate to render the production of various items tedious and expensive but also operate to inhibit the development of new products which cannot stand the economic burden imposed by older methods.

One such important problem in the filling of containers which has not been heretofore solved in a simple manner, is the problem of charging a container with several liquids, one of which has a boiling point lower than the freezing point of the other. An illustrative case is the problem of charging a container with both an aqueous solution which freezes at about 32° Fahrenheit and a liquid of moderately low boiling point such as dichlorodifluoromethane (propellant 12) whose boiling point is -21° Fahrenheit. When a low-boiling liquid such as this is added at atmospheric pressure to a container in which a liquid such as water has been placed, it rapidly begins to boil causing a loss of valuable liquid through boil-off, splatter and frothing, and in general an interference with the smooth rapid and efficient filling of the container. The boiling and the accompanying side effects arise from the contacting of the two liquids and the rapid transfer of heat from the aqueous liquid to the low-boiling liquid. Agitation due to the act of addition, convection currents and intermixing are factors that operate in producing this effect. Reversing the procedure, that is, placing the low boiler in the container first and then adding the other liquids is of no avail since a similar underside course of events follows.

One important reason for preventing loss of the low-boiling liquid is that it is often a relatively expensive material and its loss increases the cost of the finished product. Another reason for preventing such loss is that the low boiler is often present in limited quantity and the loss may interfere with proper proportionation in the final product. Despite this, the loss of a certain amount of the expensive low boiler is often tolerated in order to permit the vapors to displace the air in the container as a flushing or purging step prior to sealing.

Heretofore, several methods have been used in order to charge a container with two such liquids. However, these previously used methods have a number of disadvantages and these disadvantages make such methods commercially unattractive. One such method is to add the aqueous solution first and then completely freeze it to a solid cake by means of an external freezing bath or chamber. Since under these circumstances, the solution freezes from the bottom and peripheral edge in toward the center, this causes the upper or contacting surface to freeze last. This type of freezing is, consequently a slow process consuming much unnecessary energy. Another disadvantage of freezing the whole aqueous solution is

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that this sometimes damages one of the constituents and where the water is part of an emulsion or solid in liquid suspension, physical breakdown of the system may occur. A second typical method requires gasifying the moderately low-boiling liquid and forcing it under pressure through and around the narrow valve stem. This is obviously another slow process carrying with it the danger of injury to the valve mechanism and is one which also requires the removal of the unmixed liquid from the dip tube. Still another process involves lifting the valve cap under conditions of a closed system and then forcing in gasified liquid under pressure. To summarize briefly, the methods presently available are either too slow or are complicated and expensive.

I have discovered, however, that a temporary, relatively thin, substantially solid anti-mixing barrier can be formed on the upper surface of a freezable liquid in a container by the addition of a small quantity of a very cold, preferably expendable, preferably very low-boiling liquid having a specific gravity less than that of the freezable liquid, and that this barrier permits the rapid addition of the moderately low-boiling liquid in its liquid state and at atmospheric pressure, without the loss of such liquid through vaporization or boil-off and without the accompanying frothing or foaming or other undesirable effects. Of course where a pressure system higher or lower than atmospheric is desired for other reasons, such may be used.

This discovery forms the basis of my invention which as will be seen provides a method for overcoming these and related problems economically and efficiently. The method operates economically in that it is simple, convenient, and of low cost. It operates efficiently in that it prevents the loss of valuable components through vaporization and boil-off and eliminates slow, time consuming operations.

It is therefore an object of this invention to provide a method for economically and efficiently combining a moderately low-boiling liquid with a freezable liquid without significant loss of the moderately low-boiling liquid through vaporization, boil-off or frothing.

It is a further object of this invention to provide a method for economically and efficiently adding a low-boiling liquid to a freezable liquid in a container without the necessity of freezing the whole mass of freezable liquid.

It is a further object of this invention to provide a method for economically and efficiently adding a low-boiling liquid to a freezable liquid in a container without the necessity of using pressurized equipment.

It is a further object of this invention to provide a method for combining a freezable liquid and a propellant in an aerosol container without significant loss of propellant in such a manner that it is not necessary to freeze the entire freezable liquid, to use pressure or to vaporize said propellant.

It is an additional object of this invention to provide a method for charging a container with a plurality of liquids wherein one liquid is to be held separate temporarily from one or more other liquids.

Other objects and uses of this invention will occur to those skilled in the art upon reading the following specifications and claims.

FIGURES 1 through 8 illustrate various stages in the filling of a container according to the method of the invention. In this method, a freezable liquid which may be chilled to a temperature near its freezing point is charged into a container by a conventional means. A small amount of a very cold liquid is then charged into the container, the cold liquid contacting the upper surface of the freezable liquid causing the upper surface of the freezable liquid to freeze, thus forming a temporary, substantially

solid, anti-mixing barrier. A prechilled liquid having a boiling point lower than the freezing point of the freezable liquid is then added to the upper surface of the frozen layer. The container is then sealed off and the barrier melted. The barrier upon melting rejoins the remainder of the original freezable liquid thus providing a container charged with both the freezable liquid and the low-boiling liquid without the undesirable effects mentioned previously. Where a dip tube or similar device is to be included in the final product, it is incorporated before the container is sealed as will be described below.

With reference to the drawing, the container 11 as shown in FIG. 1 is charged with a freezable liquid 12 by a conventional means such as filler tube 14, the freezable liquid being, for example, an aqueous solution. The freezable liquid is preferably chilled to within a few degrees of its freezing point. While the chilling may be accomplished after it is introduced, it is more often conveniently carried out by prior passage through a chilling unit such as 13. Chilling reduces the amount of liquid freezing means subsequently used. A very cold low-boiling expendable liquid such as nitrogen 15 is then introduced to the container where it floats upon the surface of the freezable liquid as shown in FIGURE 2. The floating liquid freezing means quickly freezes the upper surface of the freezable liquid into a substantially solid, anti-mixing barrier 17 as shown in FIGURE 3. The vapors of the liquid freezing means released by evaporation during the introduction to the container and the contacting of the freezable liquid fill the upper part of the container flushing the air out as shown in FIGURES 2 and 3. The liquid 18 that is to be held separate from the freezable liquid by the temporary anti-mixing barrier is then introduced to the upper surface of the anti-mixing barrier as shown in FIGURE 4, the liquid 18 being, for example, a propellant such as dichlorodifluoromethane (propellant 12) or isobutane, and the small amount of the vapors from this liquid mixing with the vapors 16 and displacing at least part of them forming the new mixed vapor 19.

The container is then sealed by a sealing means 23 and the barrier is melted as shown in FIGURES 5 and 6. Where the liquid held separate from the freezable liquid is lighter than the freezable liquid such as when the former is isobutane and the latter is an aqueous solution, the liquid held separate will float on the freezable liquid as shown in FIGURE 5. Where the liquid held separate from the freezable liquid is heavier than the freezable liquid such as when the former is propellant 12, it ends up at the bottom of the container as shown in FIGURE 6. The container may be fitted with a dispensing valve on the sealing means as shown in FIGURE 8 or with a dispensing valve 20 and dip tube assembly 22 as shown in FIGURE 7. The dip tube, if used, is incorporated prior to the melting of the barrier by one of the methods described below but not shown here.

The drawing just described is provided as an aid in understanding the application of the invention to the filling of a container. The shape of the container, the liquids and their proportions as well as the style of the finished dispenser are for the purpose of illustration and are not meant to convey any limitations beyond those provided by the rest of the specification.

A number of liquids are suitable for use as a freezable liquid in this method. Typically they have melting points ranging from about -70° to 70° Fahrenheit and include such liquids as water, diacetone alcohol, carbon tetrachloride, benzene, cyclohexane, dioxane, p-xylene, and dimethylsulfoxide having melting points of 32° , -58° , -9.5° , 41.9° , 53.2° , 55.9° , and 65.3° Fahrenheit respectively. The liquids are not restricted to being pure substances, however, and are more often typically the solvent in the solution having a somewhat lower melting point than the ones shown. Other liquid media containing liquids such as the ones exemplified above are equally suitable for use in this invention including emulsions and solid in

liquid suspensions. Liquid systems containing water as a significant component are an important group of liquids that have been found to operate as the freezable liquid in this method and these include systems such as aqueous solutions, of which room deodorants are an example, oil in water emulsions, of which mayonnaise is an example, and solids in suspension, of which toothpaste is an example. The enumerations above are of course illustrative and are not meant to limit the scope of the invention.

Although a number of liquids could possibly be employed as liquid freezing means, certain properties render some of them particularly suitable for that purpose. A very low freezing point is particularly desirable so that the freezing means can be added as a very cold liquid. Since water and other liquids useful as freezable liquids in this invention often have specific gravities of one or less, liquids suitable as liquid freezing means are typically those with specific gravity less than one. A group of readily available liquids having the properties described above and coming under the scope of this invention are exemplified by nitrogen, hydrogen, helium, air, natural gas, methane and in general lower alkanes, alkenes and alkynes and mixtures thereof. It is highly preferable that the freezing means be cold enough to reduce the upper surface of the barrier to a temperature near or below the boiling point of the liquid to be added without boil-off in order to maximize the advantage of the barrier.

Another property that has been found highly advantageous in a liquid freezing means is that of having a very low boiling point. Since liquids at a temperature near their boiling point are at their lowest viscosity they may be added when they are very cold and yet at their lowest viscosity. Their low viscosity enables the liquids to spread very rapidly over the surface of the freezable liquid and thus accomplish the freezing of the upper surface quickly and efficiently. Another advantage afforded by the low viscosity is the ease of handling and pouring. An additional advantage that a very low boiling point affords a freezing means is that it causes all or most all of it to vaporize very readily during the freezing operation, thereby incorporating any residual amount in the vapor phase when it can act as an adjunct to the propellant. The ready vaporization also serves to replace and thus flush the air from a container prior to sealing. Low boiling liquids of this type which depend on heat of vaporization for cooling need no additional cooling prior to use. Those boiling below about 0° Fahrenheit being usually preferred in this method. Examples are liquid propane, boiling at -44° Fahrenheit and liquid nitrogen boiling at -321° Fahrenheit. Because of its many additional advantages such as low mammalian toxicity, non-inflammability, availability in commerce as a liquefied gas, general lack of chemical reactivity, very low solubility in most liquids and very low cost, nitrogen is a preferred material for the liquid freezing means.

The amount of liquid freezing means necessary to form the antimixing barrier varies with the cross-sectional area of the container, the particular freezable liquid involved and the actual container employed. In general I have found for instance that glass and plastic containers require the least amount of liquid freezing means, tin plate somewhat more and aluminum the most. When highly conductive materials such as aluminum are employed for the container a thin film of frozen liquid is formed wherever the freezable liquid contacts the container and this increases somewhat the requirement for liquid freezing means.

In general, the anti-mixing barrier should be of sufficient thickness in vertical cross section to support the layer of liquid which is to impose upon its upper surface making due allowance for any melting that may take place during the charging process. On the other hand, it should not be so thick as to render it difficultly frangible when it must be penetrated as described below. I have found that barriers about 0.02 to about 0.2 inch thick are satis-

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factory for most purposes, although for reasons of economy and ease of frangibility barriers about 0.03 to 0.06 inch thick are preferred.

The quantity of liquid freezing means employed while not critical, should be sufficient to freeze the upper surface of the freezable layer into a barrier which completely covers the exposed surface of the freezable liquid and which is sufficiently thick in vertical cross section to fulfill the requirements for barrier strength as explained above. The quantity of liquid freezing means employed should also be sufficient to permit the vapors to flush or purge the air from the unfilled portion of the container in the manner previously described if this action is desired. On the other hand, the quantity of liquid freezing means employed should not be so large as to be unduly wasteful or so large as to freeze the barrier into a layer too thick to permit its ready penetration by a dip tube or other member when such is to be pushed through it before it is melted.

I have found that a container which is designed to hold six fluid ounces and which is filled about two-thirds full with an aqueous solution requires about 0.2 to about 0.4 fluid ounce of liquid nitrogen to form a barrier having a thickness falling in the preferred range when the container is made of glass or plastic, about 0.4 to about 0.6 ounce when the container is made of tin-plated steel, and about 0.6 to about 0.8 ounce when the container is made of aluminum. Similar results were obtained with a water shaving cream formulation which is a water in oil emulsion and mayonnaise which is an oil in water emulsion.

One method of incorporating a dip tube in the container before melting the barrier is to push it through the frangible barrier concomitantly with the positioning of the sealing and dispensing means when the container is sealed. A sharp object may of course be pushed through the frangible barrier to aid the passage of the dip tube if desired. Another method for incorporating the dip tube is to hold the sealing and dispensing means assembly above the opening of the container while it is being charged, with the dip tube extending into the freezable liquid. When the surface of the freezable liquid is frozen it freezes around the dip tube holding it partly below the surface of the freezable liquid. When the sealing and dispensing means is positioned for sealing, this again breaks up the frangible barrier permitting the proper positioning of the dip tube.

In the following examples of the application of my invention, parts are by weight and ounces are avoirdupois unless otherwise stated.

EXAMPLE 1

Foam hair dressing

A concentrate suitable for use in a foam hair-dressing spray was prepared by admixing the following components at 160° F.:

	Parts
Stearic acid	5.56
Lanolin, anhydrous, U.S.P.	0.67
Isopropyl myristate and palmitate	4.44
Benzyl alcohol, N.F.	0.89
Mineral oil, light 65°	2.22
Polyvinylpyrrolidone	0.22
Triethanolamine	2.67
Water (distilled)	83.33

A 6-ounce tin-plated steel can lacquered on the inside was charged with 5.4 ounces of the concentrate which was cooled to about -40° F. Liquid nitrogen (0.8 fluid ounce) was introduced into the container at atmospheric pressure. After a short period a frozen layer formed on the upper surface of the concentrate. Some moisture condensation was observed on the outside of the container. A charge of 0.6 ounce of dichlorodifluoromethane was added to the upper surface of the frozen barrier without any significant foaming or boil-off occurring. The container was then sealed with a cap and valve assembly. After a short length of time it was ready for use.

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EXAMPLE 2

Foam wall cleaner

A concentrate suitable for use in a foam wall cleaner was prepared by admixing the following components:

	Parts
Nonyl phenyl polyethylene glycol (Tergitol NPX) ..	3.20
Alkyl aryl sulfonate detergent (Nacconol NSRF) ..	1.49
Tetrasodium pyrophosphate	1.00
Diethyleneglycol monoethyl ether	4.00
Water (distilled)	90.31

A 6-ounce plastic coated glass container was charged with 5.8 ounces of the concentrate which was cooled to about 40° F. Liquid nitrogen (0.6 fluid ounce) was introduced into the container at atmospheric pressure. After a short period, a frozen layer could be observed on the upper surface of the concentrate. A charge of 0.3 ounce of dichlorodifluoromethane (propellant 12) was added to the upper surface of the frozen barrier without any significant boil off or foaming. A cap and valve assembly fitted with a substantially rigid dip tube adapted to extend to within ¼ inch of the bottom of the container was pushed through the frozen barrier concomitantly with the positioning of the cap for sealing. Shortly after the sealing process the finished aerosol dispenser was ready for use.

EXAMPLE 3

A series of 6-ounce glass containers suitable for use in aerosol dispensers were charged with 4-ounce portions of the wall cleaner concentrate prepared as in Example 2. The transparent containers permitted the surface of the concentrate to be viewed quite readily. Each container was then charged with a small amount (about ½ fluid ounce) of a different cold substance. The substances included cold liquids added at a temperature slightly below their boiling points such as nitrogen, methane, propane and ethylene. They also included ethyl ether and chloroform cooled to -75° F., these being liquids cooled substantially below their boiling points and finally fine lumps of Dry Ice. The chloroform and Dry Ice were added to afford comparison with substances heavier than the concentrate. The Dry Ice sank to the bottom of the container and caused much frothing and bubbling but did not produce a frozen barrier on the upper surface of the concentrate. The chloroform sank to the bottom without any frothing but also failed to produce a frozen barrier on the upper surface of the concentrate. The ethyl ether floated on the concentrate forming a frozen barrier but the liquid ether remained floating on that barrier for some time without evaporating significantly. The nitrogen, methane, propane and ethylene all floated on the surface of the concentrate freezing it to a barrier and they evaporated during the process without leaving a liquid on top of the barrier. A polyethylene dip tube was easily pushed through the barriers thus produced.

I claim:

1. A method for economically and efficiently charging a container with a plurality of liquids comprising the steps of:
 - (a) charging a first liquid into said container,
 - (b) forming in place a temporary, destructable, substantially solid anti-mixing barrier completely covering the upper surface of said first liquid and
 - (c) charging a second liquid having a boiling point lower than the freezing point of said first liquid into the upper surface of said anti-mixing barrier whereby the heat from the first liquid is prevented from being rapidly transferred to said second liquid thus providing a container charged without the excessive loss of said second liquid through boiloff, vaporization and frothing.
2. The method of claim 1 wherein the forming in place of said barrier is accomplished by contacting the upper

surface of said first liquid with a liquid freezing means having a specific gravity lower than that of said first liquid and a temperature significantly lower than said freezing point thereby freezing said upper surface and forming said barrier.

3. The method of claim 2 wherein said first liquid is precooled to a temperature slightly above its freezing point and said liquid freezing means is a liquified gas at or near its boiling point, said boiling point being significantly lower than said freezing point.

4. The method of claim 3 wherein after the completion of said charging, the contents of said container are sealed off from the atmosphere at least temporarily and the barrier formed by freezing the upper surface of said first liquid is melted, said freezing point of said first liquid being below about 70° Fahrenheit.

5. A method of charging a container partially filled with a first liquid wherein a second low-boiling liquid is added without appreciable loss through vaporization, boil-off and frothing comprising the steps of:

- (a) contacting the upper surface of said first liquid with a volatile liquid freezing means having a much lower temperature than said first liquid thereby freezing said upper surface to a relatively thin, substantially solid, frangible, meltable barrier
- (b) introducing said second liquid to upper side of said barrier, said second liquid having a boiling point lower than the freezing point of said first liquid,
- (c) sealing off the contents of said container from communication with the atmosphere in at least a temporary manner.

6. The method of claim 5 wherein said liquid freezing means is a low viscosity liquified gas at a temperature near its atmospheric boiling point, said low-viscosity liquified gas spreading rapidly over the upper surface of said first liquid and volatilizing rapidly upon freezing of said upper surface, thereby flushing the air out of said container.

7. The method of claim 5 wherein said barrier is melted after the sealing of said container thereby permitting full contact of the first and second liquids without loss.

8. The method of claim 7 wherein said first liquid contains water in a significant quantity and is maintained at a temperature of from about 33° to 40° Fahrenheit prior to the introduction of said liquid freezing means, said liquid freezing means being a liquified gas chosen from the group consisting of nitrogen, hydrogen, helium, air, natural gas lower alkanes, alkenes and alkynes and mixtures thereof.

9. The method of claim 8 wherein said water is a component of a liquid system chosen from the group consisting of an aqueous solution, an emulsion and a colloidal solid in suspension and said liquid freezing means is nitrogen.

10. A method for economically and efficiently charging and sealing an aerosol dispenser wherein said dispenser is to be charged with a low-boiling propellant in the liquid state, comprising the steps of:

- (a) charging said unsealed dispenser with a first liquid, said liquid being essentially the material to be dispensed,
- (b) contacting the upper surface of said first liquid with a liquid freezing means having a temperature significantly below the freezing point of said first liquid, a specific gravity lower than said first liquid and being a liquified gas chosen from the group consisting of nitrogen, hydrogen, helium, air, natural gas, lower alkanes, alkenes and alkynes and mixtures thereof thereby freezing said upper surface into a temporary destructible barrier,
- (c) charging said propellant in the liquid state onto upper side of said barrier, said propellant having a boiling point lower than the freezing point of said first liquid,

(d) positioning a sealing and dispensing means on the opening of said unsealed container and effecting the seal.

11. The method of claim 10 wherein said first liquid is precooled to a temperature of from about one to ten degrees Fahrenheit above its freezing point prior to said contacting by said liquid freezing means, said liquid freezing means being a liquified gas at a temperature near its boiling point, said boiling point being significantly lower than said freezing point.

12. The method of claim 11 wherein said first liquid contains water in significant quantity, said liquid freezing means is nitrogen, and said frangible layer is melted subsequent to said sealing thereby permitting full contact of said first and second liquids.

13. The method of claim 10 wherein said destructible barrier is a thin, frangible layer, said sealing and dispensing means includes a dip tube means adapted to extend to the vicinity of the bottom of said dispenser, and said frangible layer is pierced subsequent to the charging of said propellant, thereby permitting said dip tube means to extend to the vicinity of the bottom of said dispenser concomitantly with the positioning of said sealing and dispensing means.

14. The method of claim 10 wherein said sealing and dispensing means includes a dip tube means adapted to extend therefrom to the vicinity of the bottom of said dispenser, said sealing and dispensing means being held somewhat above the unsealed opening of said dispenser while still extending said dip tube means into said first liquid during said charging and freezing steps, said dip tube means being extended to the vicinity of the bottom of said dispenser concomitant with the positioning of said sealing and dispensing means.

15. A method for charging a container with a plurality of liquids wherein one liquid is to be held separate temporarily from one or more other liquids comprising:

- (a) charging a container with a liquid to be held separate from the others,
- (b) contacting and freezing the entire upper surface of said liquid with a very cold liquid freezing means having a specific gravity lower than said charged liquid thereby forming in place a temporary, destructible, substantially solid, anti-mixing barrier,
- (c) charging the remainder of said other liquids onto upper surface of said anti-mixing barrier,
- (d) sealing off contents of said container from communication with the atmosphere,
- (e) melting said anti-mixing barrier thereby permitting admixing of said first liquid with the others.

16. A method of charging a container comprising:

- (a) introducing a freezable first liquid into said container,
 - (b) contacting the upper surface of said first liquid with a very cold highly volatile second liquid having a specific gravity less than said first liquid and being sufficiently cold to reduce the temperature of the upper surface of the barrier to a very low temperature,
 - (c) introducing to the upper surface of said barrier a third liquid having a boiling point lower than the freezing point of said first liquid and not significantly higher than the temperature of the upper surface of said barrier.
17. The method of claim 16 in which said second liquid is nitrogen.

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