COMPOSITION FOR AEROSOL DISPENSER CONSISTING OF TWO IMMISCIBLE LIQUID PHASES

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Filed Mar. 15, 1961, Ser. No. 96,013

20 Claims. (Cl. 222—394)

Our invention relates to the dispensing of liquids from containers under pressure by means of vaporization of a propellant within the container. More particularly, our invention relates to self-propelled dispensing of a liquid in the form of a substantially non-flammable spray by means of a dispenser employing a valve of particular design and containing a two-phase fluid system comprising a propellant vapor phase, a propellant liquid phase and a liquid aqueous phase or composition to be dispensed.

In self-propelled liquid dispensing systems, it is very desirable for economic reasons to utilize water as a medium for carrying the active ingredient to be dispensed but the systems that have been developed suffer from many disadvantages. It is known, for example, to utilize water in a two-phase system comprising propellant vapor and an emulsion of propellant and aqueous liquid to be dispensed. Such systems, however, may produce many sprays which are objectionable for some purposes and leave residues which may be objectionable. Also, the emulsion in many instances is too unstable to insure a uniform spray. Also, two-phase systems are known in which the propellant is solubilized in water by means of a suitable co-solvent such as an alcohol. However, due to the limited mutual solubility of the propellant and water, the amounts of water and propellant that can be used together are limited. Where the amount of propellant is large enough to give a desirable spray, the amount of water must necessarily be small to achieve a compatible system making the system less desirable from an economic point of view. On the other hand, if the amount of water is large, the amount of propellant must necessarily be small resulting in a very wet spray which is undesirable for many applications, e.g., hair sprays. Thus, substantial amounts of water cannot be employed in two-phase systems and suitable finely atomized sprays achieved. Also, such systems are costly since they require a relatively large amount of propellant. An amount of propellant in large excess of that required to expel a given quantity of the liquid composition to be dispensed must be charged to the system since a substantial quantity of propellant, in solution or emulsion with the liquid composition to be dispensed, is expelled along with the liquid composition. The amount of propellant in two-phase systems normally ranges from 50 to 70 weight percent to achieve fine degrees of atomization. If a valve is used which provides for extrusion of the liquid aqueous phase, i.e., the dip tube, must be cut short to a length just above the propellant layer on the bottom to avoid extrusion and loss of the propellant. As the container is emptied, however, the layer of propellant diminishes rapidly and is replaced by an equal volume of the liquid aqueous phase. Because of the shortness of the dip tube, when the propellant is exhausted there remains a layer of concentrate equal in volume to the original volume of the propellant and, thus, the container cannot be completely emptied. Also, propellant vaporization promoters are required for such systems. The spray pattern of such systems is somewhat wet and if a valve is used which provides admixing of propellant vapor with liquid aqueous phase to provide better atomization, because of propellant vapor loss more propellant is required which requires further shortening of the dip tube and thus even more concentrate is left in the container.

It is also desirable for economic reasons to use hydrocarbon propellants, e.g., isobutane, which are much less expensive than the halogenated hydrocarbon propellants but the flammability of the hydrocarbon propellants is a drawback to their use.

Our invention provides self-propelled liquid dispensing utilizing a three-phase system with a relatively small amount of comparatively inexpensive flammable hydrocarbon propellant and in which one of the phases is a liquid aqueous phase which can be evenly and completely dispersed to provide a non-flammable spray of the liquid aqueous phase and which also provides a choice of desired atomization ranging from a coarse wet spray to a fine dry spray. Also, our invention provides, where desired, non-foaming sprays which are particularly advantageous for hair sprays.

As embodied in a dispensing device, our invention comprises a self-propelled liquid dispensing device including a container containing under pressure a top vapor phase comprising hydrocarbon propellant vapor, a liquid propellant phase comprising liquefied hydrocarbon having a density substantially less than and being sufficiently immiscible with a bottom liquid aqueous phase so that a distinct propellant layer is maintained on the top of the bottom liquid aqueous phase during dispensing, and a valve member associated with the top of the container which includes means for admixing liquid aqueous phase and vapor from the top vapor phase prior to discharge from the container in the form of a spray.

We have found that to provide a uniform spray pattern and complete emptying or extrusion of the liquid aqueous phase and propellant from a dispenser containing three phases in a non-flammable spray, not only must a valve of the type described be used but also the liquid propellant density must be substantially less than that of the liquid aqueous phase and also the propellant must be sufficiently immiscible with the liquid aqueous phase so that a distinct propellant layer or reservoir is maintained in the dispenser on top of the bottom liquid aqueous phase during dispensing, and further the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir must be maintained within certain critical limits.

The propellants useful in our invention are normally gaseous hydrocarbons having a density in liquid phase substantially less than that of the liquid aqueous phase and sufficiently immiscible with the liquid aqueous phase so that a distinct propellant layer is maintained and in particular are isobutane, n-butane, propane and mixtures
thereof. Isobutane and n-butane are particularly preferred. Small amounts, e.g., 5 weight percent, of other hydrocarbons, such as pentane and hexane, and halogenated hydrocarbons, such as the Freons, can be used in admixture with the butanes and propane, if desired, providing the required density of the propellant liquid phase is maintained.

A liquid-liquid phase, which contains the active ingredient to be dispensed, can be water or a solution of water and an alcohol containing up to 85 weight percent alcohol. The useful alcohols are ethyl alcohol and isopropyl alcohol, with ethyl alcohol being highly preferred. When the amount of alcohol is greater than 85 percent by weight, large amounts of propellant are dissolved in the hydroalcoholic phase which adversely affects the fluidity of the spray and also can destroy the three phase system by becoming completely solubilized in the hydroalcoholic phase. The preferred amount of alcohol to provide a finely atomized, quick drying, dry spray is between 60 and 70 weight percent.

The densities of the liquid propellant phase and liquid aqueous phase must be sufficiently different so that the two phases are maintained as separate layers which are not dispersed by ordinary handling of the dispenser. The density of the liquid propellant phase should be at least 0.272 gram per cc, preferably at least 0.272 gram per cc less than the density of the liquid aqueous phase for maintenance of this condition. For example, in a system of our invention where the density of the liquid aqueous phase is 1.000 at 60° F. and the propellant is isobutane with a density of 0.564 at 60° F., the difference in densities is 0.436. In a hydroalcoholic system where the density of a hydroalcoholic phase containing 70 percent alcohol by weight is 0.835 and the propellant is isobutane, the difference is 0.271, and in a system containing less alcohol the difference is greater. Such differences provide separate layers not dispersed by ordinary handling.

The volume to volume ratio of liquid aqueous phase to liquid propellant reservoir in the case where the liquid aqueous phase is water must be between 2.95 and 3.6:1 for complete emptying of the container contents but can vary between 2.75 and 3.78:1 since at these limits acceptable amounts of propellant or concentrate remain. Where the liquid aqueous phase is a hydroalcoholic phase, the corresponding ratio is between 2.03 and 2.23:1 and between 1.8 and 2.42:1 where the weight percent of alcohol in the hydroalcoholic phase is between 20 and 85 percent, which does not affect the viscosity of the system to the extent where the ratios are affected. When the weight percent of alcohol in the liquid aqueous phase is less than 20 percent and approaching zero percent, lesser amounts of propellant are required for extrusion and as the amount of alcohol decreases the ratio of liquid aqueous phase to propellant reservoir increases until it approaches that of a 100 percent aqueous system, i.e., the corresponding ratio will be between 2.42:1 and 2.75:1 and between 2.23:1 and 2.95:1. The ratio, therefore, for uniform and complete practical extrusion for systems containing from 0 to 85 weight percent alcohol is between 1.8:1 and 3.78:1. These ratios provide even and complete emptying with a relatively small amount of propellant, e.g., 25 weight percent as compared to 40 to 85 weight percent of halogenated hydrocarbon propellant in two phase systems for finely atomized dry sprays.

By maintaining these liquid aqueous phase to liquid propellant reservoir ratios and with the valve member described above, even and complete emptying or extrusion of the liquid aqueous phase and propellant from the container in non-flammable spray is obtained without the necessity of shaking the dispenser or container. The drawback of the dispenser is to be avoided since it upsets the volume ratio of liquid aqueous phase and liquid propellant reservoir which results in incomplete emptying of the dispenser. For example, when the container is shaken thor-
tion with the hollow stem 7 and containing an orifice 17. When the valve member is actuated by pressing down the button 16, as shown in FIGURE 2, the valve 8 is unseated and the pressure of the propellant vapor extrudes the liquid aqueous phase up the dip tube 14 and through the tailpiece orifice 13 into the chamber 19 formed by housing 11. Also, at the same time vapor from the top vapor phase 2 enters the chamber through the vapor tap opening 15 and the vapor and liquid aqueous phase are intermixed in the chamber. This mixture enters the valve stem 7 through stem orifice 18 (communicating with the hollow stem passageway) and is discharged from the chamber formed by the hollow valve stem 7 through the button orifice 17 as a spray. Additional mixing occurs in the chamber formed by the hollow valve stem.

In FIGURE 3, a modification of the valve member 6 of FIGURE 1 is illustrated by a partial sectional view. The valve member of FIGURE 3 differs from that of FIGURES 1 and 2 only in that the valve housing 11a of FIGURE 3 has a tailpiece 12a with a pierced or molded orifice 13a with a minimal length, e.g., 0.030 inch, whereas the valve housing 11 of FIGURES 1 and 2 has a tailpiece 13 with an orifice 13 having the form of a long cylindrical passageway, e.g., 0.250 inch in length. The two types of valves, i.e., the valve of FIGURE 3 with the essentially two dimensional tailpiece orifice and the valve of FIGURES 1 and 2 with tubular tailpiece orifice, illustrate two basic types useful for the dispenser. While the valves illustrated are actuated by vertical action, valves actuated by tilting can also be used.

The flow rate of the liquid aqueous phase through the tailpiece orifice is an inverse function of the length of the orifice. Thus, the flow rate through the short orifice type valve is considerably greater than that through the long tubular orifice type. This liquid phase flow rate and the size of the vapor tap orifice are inter-related in achieving a desired spray pattern. By varying the size of the vapor tap orifice to provide greater or lesser vapor flow rate to compensate for the different liquid flow rates, spray patterns ranging from coarse wet sprays to finely atomized dry sprays can be obtained.

In the valve type having a short tailpiece orifice length (FIGURE 3) providing relatively high liquid phase flow rate, to obtain a finely atomized spray the vapor tap orifice should be larger than the tailpiece orifice. The coarse, wet spray can be obtained by using a vapor tap orifice equal to or substantially smaller than the tailpiece orifice. A finely atomized spray pattern can be obtained, for example, by using a tailpiece orifice with a diameter of 0.030 inch and a vapor tap orifice with a diameter of 0.030 inch.

In the valve type having a long tubular tailpiece orifice (FIGURES 1 and 2) providing relatively low liquid phase flow rate, to obtain a finely atomized spray the vapor tap orifice should be approximately equal to the tailpiece orifice and also should not be larger than 0.040 inch and preferably 0.030 inch in diameter. When the vapor tap orifice is substantially smaller than the tailpiece orifice, streaming takes place and when substantially larger the spray is predominantly propellant vapor. The stem orifice should be approximately equal to the vapor tap orifice for a finely atomized spray. With a stem orifice substantially smaller than the vapor tap orifice, e.g., 1/2 times smaller in diameter, the spray is somewhat wet. The button orifice has a substantial effect on the spray pattern and also on the spray rate of the product. The larger the button the greater the spray rate and the wetter the spray pattern. A button equipped with a conventional mechanical breakup device can be used to assist in giving a suitable, finely atomized spray for products requiring this type of spray pattern.

The dip tube should preferably be in the form of a capillary tube to minimize the initial burst of propellant vapor, but a valve equipped with a standard dip tube can be used with good results since the initial burst of propel-
lant is small. If a capillary dip tube is used, i.e., with an internal diameter approaching that of the tailpiece orifice of the valve, the liquid phase flow rate is decreased since in effect the tailpiece orifice is lengthened and a corresponding adjustment must be made in the size of the vapor tap orifice to maintain a desired spray pattern.

A typical example of the use of the dip tube of FIGURE 1 which provides a good, finely atomized spray pattern and spray rate suitable for a hair spray dispenser is such a valve equipped with a 0.120 inch diameter dip tube, a 0.025 inch diameter tailpiece orifice, a 0.025 inch diameter vapor tap orifice, a 0.030 inch diameter stem orifice and a 0.016 inch diameter stem button having a mechanical breakup and reverse taper. A typical example of a valve of the short orifice type of FIGURE 3 providing a similar but softer spray pattern is such a valve equipped with a 0.060 inch diameter dip tube, a 0.025 inch diameter tailpiece orifice, a 0.030 inch diameter vapor tap orifice, a 0.030 inch diameter stem orifice and a mechanical breakup actuator with a 0.020 inch diameter mechanical breakup button.

Our invention will be further illustrated by reference to the following examples.

Examples 1 to 10 relate to systems in which the aqueous phase is water and Examples 11 to 31 relate to systems in which the aqueous phase is a solution of water and ethyl alcohol. These examples show the critical nature of the volume to volume ratio of liquid aqueous phase to propellant reservoir to obtain even and substantially complete emptying in a non-flammable spray.

Example 32 illustrates the use of n-butane as a propellant.

Examples 33 to 36 illustrate products suitable for various uses.

Using isobutane as the propellant and water as the liquid aqueous phase, three phase systems such as that illustrated in FIGURE 1 of the drawing were formulated. All of these systems employed a precision valve with orifice diameters as follows: a 0.025 inch tailpiece, 0.025 inch vapor tap, 0.030 inch stem and 0.016 inch mechanical breakup, reverse taper actuator. All systems were made in clear plastic coated aerosol bottles and the ingredients were added by weight. The samples were placed in constant temperature baths at 70° F. and allowed to come to temperature equilibrium. The samples were then thoroughly shaken, allowed to stand at the specified temperatures for 24 hours, and sprayed down as follows. Each sample was sprayed for fifteen seconds at five minute intervals and returned to the constant temperature bath immediately after spraying to allow sample to come to temperature before each spray operation. All samples were weighed when full and at the end of excursion to determine amount remaining in the bottles. The volume to volume ratios were determined at equilibrium by measuring the respective volumes of the two liquid phases after shaking and standing 24 hours at the specified temperature. The flame extension of each system was determined by spraying the sample at a distance of six inches into the upper one-third of a candle flame and the flame extension measured using a calibrated stationary scale (page 40 of the L.C.C. Tariff 10 from the Chemical Specialties Manufacturers Association, Inc. Agencies and Regulations, August 19, 1958). A flame extension of over eighteen inches is considered flammable. The amount of isobutane dissolved was determined by measuring the volume of the first sample after shaking and after shaking at equilibrium. In all cases, the actuator was aligned with the curvature of the dip tube and the samples sprayed at a 45° angle to insure complete extrusion of the aqueous or hydroalcoholic phases. The term concentrate is used to indicate the liquid aqueous phase. The valve described above used in these examples was the long tubular orifice type illus-
The results show that at volume to volume ratios of liquid azeotropic phase (concentrate) to propellant reservoir of 2.5:1 (Example 9), 3.20:1 (Example 8), 3.45:1 (Example 7), and 3.60:1 (Example 6A) uniform and complete extrusion of the container contents is obtained. The results also show that at a ratio of 2.75:1 (Example 10), only 3 percent of propellant remains which is a safe acceptable amount and at a ratio of 3.78:1 (Example 6) only 9.4 percent concentrate remains which is an acceptable amount. At ratios higher than 3.78:1, as in Examples 4 and 5, undesirable amounts of concentrate remain (23.9 and 13.5%) and at ratios lower than 2.75:1, as in Examples 1, 2 and 3, unsafe amounts of propellant remain (9.2, 6.9 and 8.0%).

In the systems of these examples, the procedure of Examples 1 to 10 was repeated with the exception that a solution of water and ethyl alcohol was used as the liquid azeotropic phase.

The results (at 70° F.) are tabulated below:

### Example 11

<table>
<thead>
<tr>
<th>Percent w/w. Component in the Finished Product</th>
<th>22.9% Water 29.0% SD40 Alc. 25.9% Isobutane</th>
<th>22.9% Water 27.5% Isobutane</th>
<th>22.9% Water 29.0% SD40 Alc. 25.9% Isobutane</th>
<th>22.9% Water 27.5% Isobutane</th>
<th>22.9% Water 29.0% SD40 Alc. 25.9% Isobutane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of Conc. (Cps.)</td>
<td>2.07</td>
<td>2.27</td>
<td>2.87</td>
<td>2.87</td>
<td>2.87</td>
</tr>
<tr>
<td>Percent w/w. Alcohol in Concentrate</td>
<td>60.0%</td>
<td>80.0%</td>
<td>45.7%</td>
<td>65.7%</td>
<td>23.7%</td>
</tr>
<tr>
<td>v/v. Ratio of Concentrate to Propellant Reservoir</td>
<td>32.6% Prop.</td>
<td>35.9% Prop.</td>
<td>34.0% Prop.</td>
<td>35.9% Prop.</td>
<td>35.9% Prop.</td>
</tr>
<tr>
<td>Spray Rate—Gas/Min.</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Pressure</td>
<td>30 p.s.i.</td>
<td>30 p.s.i.</td>
<td>30 p.s.i.</td>
<td>30 p.s.i.</td>
<td>30 p.s.i.</td>
</tr>
<tr>
<td>Approx. Amount Isobutane Dissolved</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Emptying Characteristics at Equilibrium</td>
<td>3.5% Propellant Remaining, Negligible</td>
<td>3.5% Propellant Remaining, Negligible</td>
<td>4.0% Propellant Remaining, Negligible</td>
<td>1.4% Propellant Remaining, Negligible</td>
<td>4.5% Propellant Remaining, Negligible</td>
</tr>
</tbody>
</table>

*The propellant residual should decrease with decreased quantities of propellant on a volume basis up to Example 16; discrepancy probably due to either experimental or various in valve orifice.
The results show that at volume to volume ratios of liquid aqueous phase (concentrate) to propellant reservoir of 2.03:1 to 2.23:1 (Examples 15, 16, 25, 26, 28 and 29) uniform and complete, or practically complete, emptying is obtained. Also, at a ratio of 1.80:1 (Examples 12, 13 and 14) very small amounts of propellant remain (3.0, 4.0 and 1.4%) which are safe and at a ratio of 2.42:1 (Example 24) an acceptable amount of concentrate remains (8.5%). At ratios higher than 2.42:1, as in Examples 17, 21 and 22, undesirable amounts of concentrate remain (16.4, 20 and 15.6%) and at ratios lower than 1.80:1, as in Examples 11 and 31, unsafe amounts of propellant remain (8.4 and 6.9%).

The above ratios apply when the percent by weight of alcohol in the concentrate is between 20 percent and 85 percent, the ideal percentage of alcohol being between 60 percent and 70 percent by weight in the concentrate to obtain a finely atomized, quick drying, safe spray. To obtain varying degrees of dryness and spray patterns, the alcohol content in the hydroalcoholic concentrate can be reduced and the water phase increased. When the amount of alcohol in the concentrate is less than 20 percent by weight, however, the change in viscosity of the hydroalcoholic phase is insufficient to upset the ratios specified for the 20 to 85 weight percent alcohol system so that different ratios are required. When the weight percent of ethyl alcohol in the liquid aqueous phase is between 20 percent and zero percent, the ratios range from the lower limit for the water system of Examples 1 to 10 of 2.75:1 to the upper limit of the 20 to 85 percent hydroalcoholic system of 2.42:1. On the other hand, where the amount of alcohol is higher than 85 percent by weight in the concentrate, the viscosity of the hydroalcoholic phase is substantially reduced, upsetting the ratios specified.

As noted above, ethyl alcohol is highly preferred in the hydroalcoholic systems. Isopropyl alcohol can be used, however, although it tends to partition into the propellant layer or phase from the hydroalcoholic phase and adjustments must be made to compensate for this decrease in the hydroalcoholic phase, e.g., increasing the amount of isopropyl alcohol introduced into the dispenser.

Example 32

In this example, a system was prepared identical with that of Example 16 except that n-butane was employed as the propellant.

The results (at 70° F.) are as follows:

Percent w/w. of component in the finished product

Water ............................... 22.5
SD40 alcohol .......................... 52.5
Butane .............................. 25.0

Percent v/v. of concentrate to propellant reservoir

Concentrate .......................... 69.7
Propellant .......................... 30.3

Ratio v/v. of concentrate to propellant reservoir

Concentrate .......................... 2.30
Propellant .......................... 1.00

Flame extension ........................ 8"
Pressure at 70° F. (p.s.i.g.) ........ 21
Percent alcohol in concentrate by weight .... 70
Viscosity of concentrate at 70° F. in centipoises .... 2.37
Spray rate at 70° F. (gms./min.) .......... 18

Emptying characteristics at equilibrium—Extrudes completely.

The results show that uniform and complete extrusion of the container contents was obtained using n-butane as the propellant.

The basic systems of the preceding examples can be adapted for use to a wide variety of products such as hair grooming sprays, personal and room deodorants, colognes, suntan sprays, insecticides, paints, nasal sprays, and the like by the inclusion of active ingredients in
proper amounts. If the nature and amount of the active ingredient added to any of the basic systems of the preceding examples substantially increases the viscosity of the liquid aeous phase of the system, it may be necessary to adjust the ratio of liquid aeous phase to propellant reservoir, i.e., by increasing the amount of propellant, to compensate for the increased viscosity and obtain uniform and complete extraction of the contained contents. The water and hydroalcoholic systems of our invention permit the use of a wide range of active ingredients soluble in water or alcohol. The active ingredients are preferably those which are soluble in the liquid aeous phase, but suspensions or emulsions of ingredients can be employed. The water systems are particularly useful where alcohol is not desired as a component of the product such as in food products, e.g., food preservative sprays, and paints and where a coarse wet spray pattern is desired. The hydroalcoholic systems are particularly desirable in cosmetic and pharmaceutical products. For example, liquid active ingredient phases can be formulated for use as hair sprays by the inclusion in the hydroalcoholic liquid phase of proper hydroalcoholic soluble resins such as polyvinylpyrrolidone, certain copolymers of polyvinylpyrrolidone and vinyl acetate, dimethyl hydroxyformaldehyde, etc., properly plasticized and perfumed. Other products include room deodorants prepared by the inclusion of glycols, such as propylene glycol, diethylene glycol, triethylene glycol, quaternary ammonium compounds, and fragrance; insecticides by the inclusion of either hydroalcoholic soluble or emulsifiable toxicants, including pyrethrins and synergists; colognes by inclusion of suitable fragrances, in proper amounts, soluble in the hydroalcoholic system under consideration.

Examples 33 and 34
Examples of three phase systems based on Examples 15 and 29 above and useful as hair sprays are as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
<th>Ex. 33</th>
<th>Ex. 34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylpyrrolidone/vinylacetate (70/30) (69% solution in xylene)</td>
<td>6.00</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Polyvinylpyrrolidone</td>
<td>0.20</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Shellac</td>
<td>0.20</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Perfume</td>
<td>0.20</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Water, deionized</td>
<td>46.72</td>
<td>49.30</td>
<td></td>
</tr>
<tr>
<td>SD40 alcohol, anhydrous</td>
<td>25.00</td>
<td>25.00</td>
<td></td>
</tr>
<tr>
<td>Isobutane</td>
<td>25.00</td>
<td>25.00</td>
<td></td>
</tr>
</tbody>
</table>

The volume to volume ratio of liquid aeous phase to propellant reservoir is 2.03:1 in these examples. The difference in density of the propellant and hydroalcoholic phase is 0.312 and 0.271, respectively.

Using the valve described in Examples 1 to 10, these systems gave a spray rate of 24 grams/minute as compared to an average of 70 grams/minute for a conventional anhydrous product. This lower spray rate is very advantageous as it provides a longer lasting product. The pressure at 70° F. was 38 p.s.i.g. and the system had a flame extension of seven to eight inches. The systems sprayed down uniformly and practically completely in a non-foaming, finely atomized, dry spray and exhibited good hair holding properties and drying times. In the Example 34 system, residual concentrate remained because of the increased viscosity of the concentrate. By increasing the amount of propellant to 27%, so that the components were water 20.569%, SD40 alcohol 47.993% and isobutane 27.000% with the amounts of the other components remaining the same, to provide a liquid aeous phase to propellant reservoir ratio of 1.94:1, the concentrate residual was reduced to only 1.2% while the same spray properties of Example 34 were maintained.

Example 35
An example of a three phase system based on Example 16 above and useful as a room deodorant is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfume</td>
<td>0.20</td>
</tr>
<tr>
<td>Quaternary ammonium compound</td>
<td>22.50</td>
</tr>
<tr>
<td>Water</td>
<td>52.10</td>
</tr>
<tr>
<td>Isobutane</td>
<td>25.00</td>
</tr>
</tbody>
</table>

The spray of this product from a dispenser with the valve of Examples 1 to 10 is characterized by finely atomized airborne particles effective as a room deodorant. The product sprayed down evenly and completely in a non-flammable spray.

Example 36
An example of a three phase system based on Example 8 above and useful as a sanitary surface antiseptic spray is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary ammonium compound</td>
<td>0.25</td>
</tr>
<tr>
<td>Water, deionized</td>
<td>84.75</td>
</tr>
<tr>
<td>Isobutane</td>
<td>15.00</td>
</tr>
</tbody>
</table>

The volume to volume ratio of liquid aeous phase to liquid propellant reservoir is 3.20:1 and the difference in density of the propellant and aeous phase is 0.436. We claim:

1. A self-propelled liquid dispenser comprising a container containing therein under pressure a three-phase fluid system comprising a top vapor phase comprising propellant vapor, a liquid phase comprising propellant liquid below the top vapor phase, and a liquid aeous phase to be dispensed below the liquid propellant phase; the liquid propellant phase consisting essentially of a normally gaseous flammable hydrocarbon and having a density in liquid phase substantially less than that of the bottom liquid aeous phase and being sufficiently immiscible in the bottom liquid aeous phase so that a distinct liquid propellant reservoir is maintained on top of the bottom liquid aeous phase during dispensing, the hydrocarbon being selected from the group consisting of isobutane, n-butane, propane and mixtures thereof; the bottom liquid aeous phase comprising at least one active ingredient that is dispensed and a carrier selected from the group consisting of water and a solution of an alcohol in water in an amount up to about 85 weight percent alcohol, said alcohol being selected from the group consisting of ethyl alcohol and isopropyl alcohol; the volume to volume ratio of liquid aeous phase to liquid propellant reservoir being between 1.8 and 3.78:1; and a valve member associated with the top of the container for dispensing the contents of the container including means for admixing the liquid aeous phase with vapor from the top phase prior to discharge from the container.

2. The dispenser of claim 1 in which the density of the liquid propellant phase is at least about 0.25 gram/cubic centimeter less than the density of the liquid aeous phase.

3. The dispenser of claim 1 in which the propellant is isobutane.

4. The dispenser of claim 1 in which the alcohol is ethyl alcohol.

5. The dispenser of claim 1 in which the carrier is water and the volume to volume ratio of liquid aeous phase to liquid propellant reservoir is between 2.75 and 3.78:1.

6. The dispenser of claim 1 in which the carrier is a solution of an alcohol in water and the volume to volume ratio of liquid aeous phase to liquid propellant reservoir is between 1.80 and 2.75:1.
7. The dispenser of claim 1 in which the density of the liquid propellant phase is at least about 0.25 gram cubic centimeter less than the density of the liquid aqueous phase, the propellant is isobutane, the carrier is water and the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir is between 2.75 and 3.78:1.

8. The dispenser of claim 7 in which the ratio is between 2.95 and 3.6:1.

9. The dispenser of claim 1 in which the density of the liquid propellant phase is about 0.25 gram/cubic centimeter less than the density of the liquid aqueous phase, the propellant is isobutane, the carrier is a solution of ethyl alcohol in water and the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir is between 1.8 and 2.75:1.

10. The dispenser of claim 9 in which the solution of ethyl alcohol in water contains from 20 to 85 weight percent ethyl alcohol and the ratio is between 1.8 and 2.42:1.

11. The dispenser of claim 10 in which the ratio is between 2.03 and 2.23:1.

12. The dispenser of claim 1 in which the valve member includes a mixing chamber provided with openings for the separate entry of the top vapor phase and liquid aqueous phase to be dispensed into the chamber and valve means for releasing the mixture of liquid and vapor from the chamber into a valve passageway communicating with the exterior of the container.

13. The dispenser of claim 1 in which the liquid propellant phase consists of a normally gaseous flammable hydrocarbon selected from the group consisting of isobutane, n-butane, propane and mixtures thereof.

14. A two-phase composition for dispensing from a self-propelled liquid dispenser container having a valve member associated with the top of the container for dispensing the contents of the container including means for admixing a liquid aqueous phase with vapor from a top vapor phase prior to discharge from the container, the composition comprising a liquid phase comprising propellant liquid and a liquid aqueous phase to be dispensed below the liquid propellant phase; the liquid propellant phase consisting essentially of a normally gaseous flammable hydrocarbon and having a density in liquid phase substantially less than that of the bottom liquid aqueous phase and being sufficiently immiscible in the bottom liquid aqueous phase so that a distinct liquid propellant reservoir is maintained on top of the bottom liquid aqueous phase during dispensing, the hydrocarbon being selected from the group consisting of isobutane, n-butane, propane and mixtures thereof; the bottom liquid aqueous phase comprising at least one active ingredient to be dispensed and a carrier selected from the group consisting of water and a solution of an alcohol in water in an amount up to about 85 weight percent alcohol, said alcohol being selected from the group consisting of ethyl alcohol and isopropyl alcohol; the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir being between 1.8 and 3.78:1.

16. The composition of claim 15 in which the liquid propellant phase consists of a normally gaseous flammable hydrocarbon selected from the group consisting of isobutane, n-butane, propane and mixtures thereof.

17. The composition of claim 15 in which the density of the liquid propellant phase is at least about 0.25 gram/cubic centimeter less than the density of the liquid aqueous phase.

18. The composition of claim 15 in which the density of the liquid propellant phase is at least about 0.25 gram/cubic centimeter less than the density of the liquid aqueous phase, the propellant is isobutane, the carrier is water and the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir is between 2.75 and 3.78:1.

19. The composition of claim 15 in which the density of the liquid propellant phase is about 0.25 gram/cubic centimeter less than the density of the liquid aqueous phase, the propellant is isobutane, the carrier is a solution of ethyl alcohol in water and the volume to volume ratio of liquid aqueous phase to liquid propellant reservoir is between 1.8 and 2.75:1.

20. The composition of claim 19 in which the solution of ethyl alcohol in water contains from 20 to 85 weight percent ethyl alcohol and the ratio is between 1.8 and 2.42:1.

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