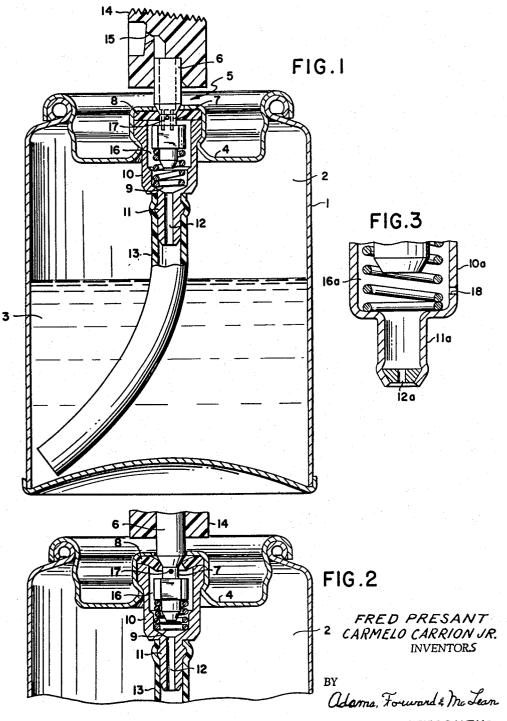
Sept. 21, 1965 F. PRESANT ETAL 3,207,386 AEROSOL DISPENSER PRODUCING NON-FLAMMABLE SPRAY WITH FLUID SYSTEM HAVING A FLAMMABLE PROPELLANT Filed June 1, 1962



ATTORNEYS

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3,207,386 AEROSOL DISPENSER PRODUCING NON-FLAM-MABLE SPRAY WITH FLUID SYSTEM HAVING A FLAMMABLE PROPELLANT

Fred Presant and Carmelo Carrion, Jr., Bridgeport, Conn., assignors to Aerosol Techniques, Inc. Filed June 1, 1962, Ser. No. 199,524 14 Claims. (Cl. 222–394)

Our invention relates to the dispensing of liquids from a container under pressure by means of vaporization of a 10 propellent 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 containing a fluid system comprising a propellent vapor phase and an essentially continuous 15 liquid aqueous phase containing an active ingredient solute to be dispensed and a flammable propellent.

In self-propelled liquid dispenser systems it is very desirable for economic reasons to utilize water as a medium for carrying the active ingredient to be dispensed. 20 It is known, for example, to utilize water in three phase stratified systems having a liquid aqueous phase, a liquid hydrocarbon propellent phase, and a propellent vapor phase. Such systems employ liquified hydrocarbon propellents, such as isobutane, propane and n-butane or 25 halogenated hydrocarbons as the hydrocarbon phase which vaporized to form the propellent vapor phase. One such system has been described in U.S. Patent 2,995,278. Systems of the type just mentioned require that the ratio of one phase to another be accurately controlled and 30 correlated with the propellent valve orifices to insure complete and even extrusion.

It is also known, for example, to utilize water in a two phase system comprising propellent vapor and an 35 emulsion of propellent and aqueous liquid to be dispensed. Such systems, however, may produce foamy sprays which are objectionable for some purposes and lease residues which may also be objectionable. Furthermore, due to viscosity limitations the emulsions employed in these systems in many instances are too unstable to insure a uniform spray. Also, they require shaking before use to produce a uniform spray. Also, two-phase systems are known in which essentially water-insoluble Freon propellents are solubilized in small amounts of water by means of a suitable co-solvent such as alcohol. Due to the limited mutual solubility of the propellent and water, however, the amount of water that can be used is very limited. Where the amount of propellent is large enough to give a desirable spray the amount of water neces-50 sarily is comparatively small thereby making the system economically undesirable. On the other hand, if the amount of water is relatively large, the amount of propellent must necessarily be small resulting in an extremely wet spray and incomplete extrusion at times. 55 Thus, substantial amounts of water cannot be employed in such two-phase systems and sprays obtained with complete extrusion of the product. Conventional hair sprays providing a finely atomized, quick drying spray pattern utilize an anhydrous two-phase system of alcohol and non-flammable, relatively expensive halogenated hydrocarbon propellent in which the amount of propellent ranges from 50 to 70 percent to achieve fine degrees of atomization.

Our invention provides self-propelled liquid dispensing utilizing a comparatively inexpensive, flammable propellent, i.e., dimethyl ether, to dispense an active ingredientcontaining liquid aqueous phase in the form of a nonfoaming, non-flammable spray containing relatively large amounts of water with complete extrusion of the liquid aqueous phase. Moreover, in accordance with our invention a finely atomized spray approaching the properties of a conventional anhydrous type spray can be obtained. 2

As embodied in a dispensing device, our invention comprises a self-propelled liquid dispenser including a container containing under pressure a fluid system comprising a propellent vapor phase and an essentially continuous liquid aqueous phase containing an active ingredient solute, water and a propellent comprising dimethyl ether, and a valve member associated with the top of the container for dispensing the contents of the container in the form of a spray. The type of spray described above produced by the dispenser of our invention is attained by maintaining certain proportions of the components of the system and maintaining certain characteristics of the valves employed. The propellent and water components of the liquid aqueous phase are in the proportions of from about 5% by weight dimethyl ether up to the limit of solubility of dimethyl ether in water (about 35% by weight) and the balance water (about 95 to 65% by weight). Within these proportions, coarse and fine spray patterns can be obtained as will be described below.

The valve member employed with the dispenser of our invention is adapted for continuous delivery of the contents of the container as opposed to metering valves which are adapted to deliver a discrete quantity of product each time the valve is actuated. The particular continuous delivery valve utilized in a specific embodiment of our invention can be either of the types described as a "vapor tap" valve or a "non-vapor tap" valve. Generally, a nonvapor tap valve is one providing communication directly from the liquid to be dispensed through a dip tube and/or tail piece, a valve means and a valve passageway to the exterior of the container. A vapor tap valve can be described as including a mixing chamber provided with separate openings for the vapor phase and the liquid phase to be dispensed into the chamber and valve means for releasing the mixture of liquid and vapor in the chamber into a valve passageway communicating with the exterior of the container.

We have found that the limits of proportions of the components of the liquid aqueous phase will vary within the broad ranges set forth above depending upon the type of spray desired. When a finely atomized anhydrous type spray is desired, it is necessary to employ at least 25% by weight dimethyl ether in water and the balance water. While either a vapor tap or non-vapor tap valve can be employed with such a system and still obtain a finely atomized spray, the employment of a vapor tap valve provides a softer type of spray. When a coarse, wet spray is desired, e.g., in a hair set spray or window cleaner, we have found that the dimethyl ether components of the liquid aqueous phase cannot be greater than about 25% by weight. Preferably a non-vapor tap valve is used since a vapor tap valve is not needed for a coarse spray, although it can be used if desired.

We have also found that the limits of proportions of the components will vary within the broad ranges to obtain complete extrusion depending on the type of valve used, vapor tap or non-vapor tap. When a non-vapor tap valve is used the minimum amount of dimethyl ether required in the liquid aqueous phase to extrude it completely is about 5% by weight. When a vapor tap valve is employed, the minimum amount of dimethyl ether required for complete extrusion is about 10% by weight.

Thus, for a non-flammable, fine spray pattern with complete extrusion the proportions are from about 25 percent by weight of dimethyl ether up to its limit of solubility in water and the balance water. For a non-flammable, coarse spray pattern with complete extrusion when employing a non-vapor tap valve the proportions are from about 5 to about 25 weight percent dimethyl ether and the balance water; if a vapor tap valve is used the proportions are from about 10 to about 25 weight percent dimethyl ether and the balance water.

We have found that depending upon which one of the two types of continuous delivery valves mentioned above, vapor tap and non-vapor tap, is employed the orifice diameters and other physical characteristics must be selected so as to provide a spray rate within the range from about 20 5 to about 100 grams per minute at 70° F. to provide a nonflammable spray. When employing a non-vapor tap valve, the orifice diameters and other physical characteristics of the valve must be selected so as to provide a spray rate within the range from about 20 to about 100 grams 10 per minute at 70° F. in order to provide a non-flammable spray. When employing a vapor tap valve, the orifice diameters and other physical characteristics of the valve must be selected so as to provide a spray rate within the range from about 20 to about 60 grams per minute. 15

In addition to the obvious economic advantages involved in employing a substantial quantity of water as a carrier together with the use of the inexpensive dimethyl ether propellent there are other significant advantages obtained through the employment of dimethyl ether in the 20 systems. The low boiling point of dimethyl ether (-24.9° C. at 760 mm. Hg) provides excellent atomization of the product dispensed and its low density (0.661 g./ml. at 20° C.) offer a comparatively large volume of propellent per unit weight. Furthermore, the 25 great solubility of dimethyl ether in water (35.3% by weight in water at 24° C. at about 5 atmospheres) affords a compatible system and further assists in the atomization of the water particles upon release. Since the water and dimethyl ether are present in a single, continuous phase 30 in the dispenser of our invention, the dimethyl ether is not only present in the dispensed spray, where it assists in the atomization of the product, but due to its presence in the liquid aqueous phase also serves as a co-solvent for the active ingredient along with the water. Thus, the 35 function of the dimethyl ether is twofold, that of assisting in solubilizing the active ingredients into the system as well as acting as a co-solvent for other water insoluble ingredients which might be incorporated into the system. Besides the advantages mentioned above, dimethyl ether 40 is also non-corrosive to metals, non-toxic, stable in the presence of heat and moisture, and relatively inert chemically.

Our invention will be further illustrated by reference to the accompanying drawing.

FIGURE 1 is a vertical cross-sectional view of a pressure container in which the two phases are illustrated as well as a non-vapor tap dispensing valve, in closed position, of the dispenser of our invention.

FIGURE 2 is a view similar to FIGURE 1 showing 50 the valve in open or dispensing position.

FIGURE 3 illustrates a modification of the dispensing valve of FIGURES 1 and 2, i.e., a vapor tap valve.

In FIGURE 1, the dispenser comprises a closed container 1 in which is contained a top vapor phase 2 com-55 prising vaporized propellent, a continuous aqueous phase. 3 containing an active ingredient, water and liquified dimethyl ether propellent. The container 1 can be made of glass, plastic coated glass, plastic materials, aluminum, tin plated steel, and stainless steel. Corrosion inhibitors 60 can be included in the liquid aqueous phase to inhibit corrosion of metal containers. The container 1 is provided with a cup member 4 for holding a valve member 5 in the top of the container for dispensing the contents of the container. The valve member 5 comprises a 65 hollow stem 6 with the valve 7 normally seated against gasket surface 8 by means of spring 9 (in FIGURE 1 the value is shown in closed or non-dispensing position). Surrounding the valve is a housing 10 (also known as the spring cup or valve body) with a tailpiece 11, with open-70ing or orifice 12. Attached to the tailpiece 11 is dip tube 13 extending into the liquid aqueous phase. On the valve stem 6 is mounted an actuator or button 14 containing a passageway in communication with the hollow stem 6 and containing an orifice 15. When the valve member is 75 reference is made to the following examples:

actuated by pressing down the button 14, as shown in FIGURE 2, the valve 7 is unseated and the pressure of the propellent vapor extrudes the liquid aqueous phase up the dip tube 13 and through the tailpiece orifice 12 into the chamber 16 formed by housing 10. The liquid aqueous phase being dispensed then enters the valve stem 6 through stem orifice 17 (communicating with the hollow stem passageway) and is discharged from the chamber formed by the hollow valve stem out through the button orifice 15 as a spray.

In FIGURE 3 two modifications of the valve member 5 of FIGURE 1 are illustrated by a partial sectional The valve member of FIGURE 3 differs from that view. of FIGURES 1 and 2 in that valve housing 10a of FIG-URE 3 has an opening or orifice 18 for the separate entry of vapor from the top vapor phase 2 and a tailpiece 11a with a pierced or molded orifice 12a with a minimal length, e.g., 0.030", whereas the valve housing 10 of FIG-URES 1 and 2 has a tailpiece 11 with an orifice 12 in the form of a long cylindrical passageway, e.g., 0.250" in length. As explained above in relation to FIGURES 1 and 2, when the valve member is actuated, the valve is unseated and the pressure of the propellent vapor extrudes the liquid aqueous phase up the dip tube and through the tailpiece orifice into the chamber formed by the housing. In the modification illustrated in FIG-URE 3 vapor from the top vapor phase 2 enters the chamber 16a through the vapor tap opening 18 at the same time that the liquid aqueous phase is introduced into the chamber 16a and the vapor and liquid aqueous phase are intermixed in the chamber 16a. This mixture then passes into the hollow valve stem where further mixing occurs.

The flow rate of the liquid aqueous phase through the tailpiece orifice is inversely proportional to the length of the orifice. Thus, the flow rate through the short orifice type valve of FIGURE 3 is considerably greater than through the long tubular orifice type valve of FIG-URES 1 and 2. This liquid phase flow rate and the size of the vapor tap orifice are interrelated in achieving the 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. While FIGURE 3 shows a valve employing both a vapor tap opening 18 and a minimal length tailpiece orifice 12a, it will be understood, of course, that either of these two modifications can be employed alone.

In fact, when a coarse wet spray is desired, a vapor tap valve is generally not employed. In addition to the employment of long or short tailpieces and vapor tap or non-vapor tap valves to control flow rates and spray patterns the spray rate can also be reduced by employing a capillary dip tube.

The compositions of our invention can be prepared and dispensers filled with them by means known to the art, e.g., pressure filling a suitable container. For example, the active ingredient in proper amount can be dissolved in the water component of the liquid phase and the resulting solution added to an open container, or water can be first introduced into an open container and the active ingredient added and the container then sealed with a closure having a dispensing valve. A large cylinder or another aerosol container containing the dimethyl ether under pressure is then connected to the container to be charged. The dimethyl ether is charged to the dispensing container through the container valve and dissolved in the liquid aqueous phase. The quantity of propellent charged to the container can be regulated, for example, by separating a discrete measured quantity of propellent and charging merely this quantity to the container.

In order to illustrate our invention more completely

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EXAMPLE I

In this example a two-phase system was employed comprising a propellent vapor phase and a continuous liquid aqueous phase containing dimethyl ether propellent in which the proportions of water and dimethyl ether in the liquid aqueous phase were 65% by weight and 35% by weight, respectively. The valve employed with the container in this example was a non-vapor tap Precision valve with the following orifice diameters: 0.080'' body, 0.013'' stem and 0.016'' mechanical breakup, reverse taper button. The sample of this example was placed in a constant temperature bath at 70° F. and allowed to come to temperature equilibrium. The sample was then shaken, allowed to stand for 24 hours and then sprayed.

The flame extension was determined by spraying the sample at a distance of 6 inches into the upper 1/3 of a candle flame and the flame extension measured using a calibrated stationary scale (ICC Tariff 13, September 25, 1960). A flame extension of over 18 inches is considered 20 flammable.

The open drum test was conducted by placing a 55 gallon metal drum on its side and positioning a candle or microburner midway between the open end and the bottom of the drum. The sample was then sprayed into 25 the drum for 60 seconds. If any of the vapors are ignited or if the flame is significantly lengthened, the sample is considered flammable. (ICC Tariff 13.)

The closed drum test is conducted substantially in the same manner as the open drum test with the exception ³⁰ that the drum is closed by a hinged lid. Three spray entry ports are drilled in one end of the drum and the sample sprayed for 60 seconds through such ports. If an explosion or pressure pop occurs with sufficient force to swing out the hinged lid, the product is classed as ³⁵ flammable. (ICC Tariff 13.)

Table I

	Example I	
Water	percent 65	40
Dimethyl ether	percent35	
Pressure at 70° F.	p.s.i.g 58	
Spray rate at 70° F.	gm./min 45	
Spray pattern	Fine	1
Flame extension	None	45
Drum tests	Passes	

From the foregoing tests it can be seen that the liquid aqueous phase of this system can contain up to about 35% by weight dimethyl ether and still provide a nonflammable spray with a non-vapor tap valve when operating at the spray rate indicated. The system of this example provides a finely atomized spray approaching the anhydrous type although it is not as quick drying as an anhydrous spray. The liquid aqueous phase of this example was completely extruded from the container. ⁵⁵

EXAMPLES II AND III

In the systems of these examples the procedure of the preceding example was repeated with the exception that a vapor tap valve was employed. The valve was a Precision valve having the following orifice diameters: 0.050" capillary dip tube, 0.020" vapor tap, 0.018" stem and a 0.016" mechanical breakup, straight taper button Type A.

	Example II	Example III	
Water (wt. percent)	72	65	7
Dimethyl ether (wt. percent)	28	35	
Pressure at 70° F	52	58	
Spray rate (grams/minute)	27.6	25	
Spray pattern	Fine	Fine	
Drum tests	Passes	Passes	
Flame extension	None	None	

From these examples it can be seen that a system 75

employing a vapor tap valve and up to about 35% by weight dimethyl ether will yield a non-flammable spray when operating at the spray rates shown. Although the sprays of these examples are not quick drying, they are sprays approaching the anhydrous type. The liquid aqueous phase in both of these examples was completely extruded from the containers.

The basic systems of the preceding examples can be adapted for use to a wide variety of products such as 10 certain hair grooming sprays, paints, window cleaner sprays, foods, nasal sprays, and the like by the inclusion of active ingredients in proper amounts. The waterdimethyl ether system of our invention is particularly desirable in some cosmetics and paints where a slightly 15 wet to a coarse, wet spray pattern is desired. For example, liquid active ingredient phases can be formulated for use as hair set sprays using a vapor tap valve by the inclusion in the liquid aqueous phase of water soluble resins such as polyvinyl pyrrolidone, certain co-polymers 20 of pyrrolidone and vinyl acetate, dimethyl hydantoin

formaldehyde, etc., properly plasticized and perfumed. The following examples based on the above systems illustrate several systems in accordance with our invention employing a variety of active ingredients.

EXAMPLE IV

An illustration of a system useful as a non-alcoholic spray bandage for burns is as follows:

Formulation:	Percent w./w.
Polyvinylpyrrolidone/vinyl acetate .	3.0
Water	67.0
Dimethyl ether	30.0

The valve employed with this system was a vapor tap Precision valve having the following orifice diameters: 0.050" capillary dip tube, 0.020" vapor tap, 0.018" stem and 0.016" mechanical breakup straight taper button, Type A.

The liquid aqueous phase of this system was continuous and the spray of this product was characterized by a finely atomized spray approaching conventional anhydrous type products. The product sprayed down evenly and was extruded completely as a non-flammable spray.

EXAMPLE V

An illustration of a system useful as a wave set spray is as follows:

Formulation:	Percent w./w.
Polyvinylpyrrolidone	2.14
Acetyl triethyl citrate	
Perfume	0.20
Inhibitor	0.20
Water, deionized	82.24
Dimethyl ether	15.00

The valve employed was a vapor tap Precision valve having the following orifice diameters: 0.060" capillary dip tube, 0.013" vapor tap, 0.018" stem, 0.016" mechanical breakup reverse taper button.

The spray of this product gives a coarse wet spray. 60 This system had a pressure of 36 p.s.i.g. at 70° F. and a spray rate of 52 grams per minute at 70° F. The product sprayed down evenly and was completely extruded as a non-flammable spray. As mentioned above, a vapor tap valve is not necessary when a coarse wet spray is desired 65 and a non-vapor tap valve could have also been employed with the system of this example.

EXAMPLE VI

An illustration of a system useful as a window cleaner 70 is as follows: Formulation:

ermulation: Percent w	7./w.
Butyl carbitol	5.0
Water	84.8
Inhibitor	07.0
Dimethyl ether	10.0

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The valve employed was a non-vapor tap Precision valve having the following orifice diameters: 0.080'' body, $4 \times 0.025''$ stem, 0.016'' mechanical breakup straight taper button, Type A.

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This system has a pressure of 25 p.s.i.g. at 70° F. and 5 provided a spray rate of 60 grams per minute at 70° F. The spray of this product gives a coarse wet spray. The product sprayed down evenly and was extruded completely as a non-flammable spray. If it were desired, a vapor tap valve could also have been employed in the 10 system of this example to provide a coarse wet spray.

We claim:

1. A self-propelled liquid dispenser comprising a container containing therein under pressure a fluid system comprising a propellent vapor phase and a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water, and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 5% by weight dimethyl ether up to 20 the limit of solubility of dimethyl ether in water and the balance water, and a valve member associated with the container adaptable for continuous dispensing of the contents of the container at a spray rate providing a substantially non-flammable spray. 25

2. A self-propelled liquid dispenser comprising a conprising a container containing therein under pressure a fluid system comprising a propellent vapor phase and a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water 30 and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 25% by weight dimethyl ether up to the limit of solubility of dimethyl ether in water and the balance water, and a valve member associated with the container adaptable for continuous dispensing of the contents of the container at a spray rate providing a substantially non-flammable spray.

3. The dispenser of claim 2 in which the valve member is a vapor tap valve.

4. The dispenser of claim 2 in which the valve member is a non-vapor tap valve.

5. A self-propelled liquid dispenser comprising a container containing therein under pressure a fluid system comprising a propellent vapor phase and a continuous 45 liquid aqueous phase containing active ingredient and a carrier consisting essentially of water and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 5 to about 25% by weight of dimethyl ether and the balance water, and a non-vapor tap valve member associated with the container adaptable for continuous dispensing of the contents of the container at a spray rate providing a substantially non-flammable spray.

6. A self-propelled liquid dispenser comprising a containing therein under pressure a fluid system comprising a propellent vapor phase and a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 10 to about 25% by weight of dimethyl ether and the balance water, and a vapor tap valve member associated with the container adaptable for continuous dispensing of the contents of the container at a spray rate providing a substantially non-flammable spray.

7. The dispenser of claim 1 in which the spray rate is within the range from about 20 to about 100 grams per minute at 70° F.

8. The dispenser of claim 3 in which the spray rate is 70 within the range from about 20 to about 60 grams per minute at 70° F.

9. The dispenser of claim 4 in which the spray rate is within the range from about 20 to about 100 grams per minute at 70° F.

10. The dispenser of claim 1 in which the valve member is a vapor-tap valve member including a mixing chamber provided with openings for the separate entry of the propellent vapor phase and liquid aqueous phase to be dispensed into the chamber and valve means for releasing the mixture of liquid and vapor in the chamber into a valve passageway communicating with the exterior of the container.

11. A composition for dispensing from a self-propelled liquid dispenser and maintained under pressure in a container having a valve member associated with the container adaptable for continuous dispensing of the contents of the container, the composition comprising a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 5% by weight dimethyl ether up to the limit of solubility of dimethyl ether in water and the balance water.

12. A composition for dispensing from a self-propelled liquid dispenser and maintained under pressure in a container having a valve member associated with the container adaptable for continuous dispensing of the contents of the container, the composition comprising a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water and a propellent components of the liquid aqueous phase being in the proportions of from about 25% by weight dimethyl ether up to the limit of solubility of dimethyl ether in as water and the balance water.

13. A composition for dispensing from a self-propelled liquid dispenser and maintained under pressure in a container having a non-vapor tap valve member associated with the container adaptable for continuous dispensing of the contents of the container the composition comprising a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 5 to about 25% by weight of dimethyl ether and the balance water.

14. A composition for dispensing from a self-propelled liquid dispenser and maintained under pressure in a container having a vapor tap valve member associated with the container adaptable for continuous dispensing of the contents of the container, the composition comprising a continuous liquid aqueous phase containing an active ingredient and a carrier consisting essentially of water and a propellent comprising dimethyl ether, the water and propellent components of the liquid aqueous phase being in the proportions of from about 10 to about 25% by weight of dimethyl ether and the balance water.

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RAPHAEL M. LUPO, Primary Examiner.

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,207,386

September 21, 1965

Fred Presant et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 37, for "lease" read -- leave --; column 7, lines 26 and 27, strike out "a conprising".

Signed and sealed this 7th day of June 1966.

(SEAL) Attest:

ERNEST W. SWIDER Attesting Officer EDWARD J. BRENNER Commissioner of Patents