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3,218,263 GELLED PROPELLENT FOR AEROSOL DISPENSERS

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The present invention relates to a gelled propellant for use in an aerosol type apparatus capable of dispensing a dry spray of an active powder in a substantially liquid-free stream of a propellant gas.

Aerosol type containers have achieved a great deal of popularity as means for dispensing a fluidized product. For example, such products as insecticides, agricultural compositions, anti-perspirants, body powders and medicant powders are widely used in such a manner. The possible applications to which an aerosol system might be applied are virtually numberless. Normally though, the most common systems utilize a propellant gas or liquid at least partially dissolved in an active liquid to be dispensed. When the dispensed material leaves the container in liquid form usually there is no problem encountered. Such a container charge usually takes the form of a mixture made up of the dispensed liquid and the propellant. Similarly, when a powder is to be dispensed, the slurry-type of mixture may be employed but only to a limited extent.

Operationally, dispensing a dry powder in one of the above noted manners involves several problems. Primary among such problems is clogging of the container valve. Also, agglomerating of the powder both in the container and in the valve sections tends to decrease the value of this dispensing means. Furthermore, there are instances when even minute particles of the propellant in liquid phase would be undesirable in the dispensed stream. Notably, in the treatment of foods or open wounds with an aerosol dust, the presence of liquid would be prohibitive.

The industry has attempted in many ways to overcome these problems and devise means for satisfactorily delivering a powder. Among these means is closer control of the powder particles. A further device resorted to in the industry is to provide especially constructed containers, or aerosol bombs as they are frequently referred to, in which the powdered materials and the propellant are separately stored prior to activation of the control valve.

It is readily appreciated that since much of the value of an aerosol system lies in the expendability of the container, any factor which increases the cost of this item is economically impractical. It is therefore a primary objective of the invention to provide an aerosol system for use in a pressurized container adapted to dispensing active ingredients in a substantially liquid-propellant-free carrier stream.

A further object is to provide a composition for use in an aerosol-type dry powder dispenser which composition includes a liquefiable propellant being present in the composition in a gelled consistency.

In brief, what is contemplated by the present invention is a propellant charge for use in an aerosol-type of container, said charge consisting of a vaporizable liquid, said liquid being present in sufficient amount to discharge in a liquid-propellant-free stream the contents comprising an active ingredient held in a container, and a thickening agent intermixed with and dispensed through said liquid in sufficient amount to form a homogeneous gelled composition therewith.

For the purpose of clarifying the following discussion, the term gel will be used to define the disclosed composi-

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tion in phraseology familiar to the art. A gel is defined in Industrial Chemistry of Colloids and Amorphous Materials, Lewis, W. K., et al., The MacMillan Company (1943), pg. 225 as: A mixture, one component of which is a fluid, homogeneous down to substantially colloidal dimensions, capable of resisting a definite shearing force.

The aerosol-type container or aerosol bomb in which the gelled propellant is normally employed is a familiar item both in the home and in industry. Such a container, when utilized for ejecting a dry powder spray, may be adapted to hold the dry powder and the gelled propellant. The majority of aerosol containers, in accordance with present practices, are constructed to withstand internal pressures of at least about 70 p.s.i.g. Such containers for practical purposes are relatively small and normally actuated through a pushbutton-type, pressure release valve communicated with the container interior usually by means of a dip-tube in order to discharge the contents.

In addition to its capability to propel the contents of an aerosol bomb upon release of pressure within the bomb, the gelled propellant composition is ideally suited for charging aerosol-type containers. In such a charging process suitable metered amounts of the gelled propellant could be placed in an aerosol container already containing the active material charge and the container capped immediately thereafter.

Among the liquid propellents which find wide usage in the present-day aerosol systems are the vaporizable fluorocarbon propellents. These propellents include, for example, trichloromonofluoromethane (Ucon 11), dichlorodifluoromethane (Ucon 12), monochlorodifluoromethane (Ucon 22), and dichlorotetrafluoroethane (Ucon 114). The internal container pressure generated by these propellents when confined at about room temperature, falls broadly within a range of from about 10 to 70 p.s.i.g. When Ucon 12 provides the propelling medium, the vapor pressure at 70° F. will be about 70 p.s.i.g. To attain a lesser internal pressure, a mixture of various propellents will lower the pressure generally in proportion to the particular mixture of propellents employed.

The main criterion for effective gelling or thickening of a liquid gas into a gelled consistency is the particle size of the thickening agent. Most satisfactory gels are obtained if the thickening agent particles are of colloidal dimensions (between about 1 and 100 millimicrons). However, it has been found that satisfactory gels or thickened propellents are obtainable by using a powdered thickener having a particle size of 44 microns or less (i.e., passing through a U.S. Std. No. 325 mesh sieve). Generally, compositions containing particles as large as about 10³ microns cannot be classified as gels because of the relatively large particle size; however, the use of such particles results in a thickened mass suitable for use in dry powder or dust aerosol systems.

The term "colloidal dimension" herein used, arbitrarily describes chosen particle size limits between about 1 and 100 millimicrons. The upper limit in each instance being dependent on the particular system, usually being the maximum particle size which will not settle out from the suspending media.

A further requisite for the preferred gelling agent is the presence of amorphous silica in the composition. It has been found that an agent containing amorphous silica or a siliceous material is highly beneficial to the mixture. For example experimentation has shown that the most preferred embodiments of thickening agents are those containing colloidal-size particles including amorphous silica in an amount of at least 95 percent by weight.

It has been found furthermore that there exists a definite correlation between the gelation tendency of a liquefied propellant and its Trouton number in the instance of a silica-type gelling agent. Generally, a condition of gela-

tion can be achieved with a liquefied propellant having a Trouton number less than or equal to 21.

For the purpose of the following description, the Trouton number of a vaporizable propellant is defined as L_e/T_b where L_e denotes the molar heat of vaporization of the liquid in calories per gram-mole T_b denotes the boiling point of the liquid at normal atmospheric pressure in degrees Kelvin. Illustrative of this characteristic, the Trouton numbers of several widely used propellants are here listed. Trichlorofluoromethane has a Trouton number of 20.3; dichlorodifluoromethane 19.9; and dichlorotetrafluoroethane 20.0.

To determine the thickening properties of various finely divided substances, the following procedure was used. A quantity of the powdered test specimen was measured into a plastic-coated pressure container (Wheaton bottle). The contents of the bottle were then supersaturated with the liquid propellant being tested. The mixture was then boiled until by observation it was seen that the mixture had assumed the form of a stable gel. This condition of stability, for the purpose of the test, was determined to be as follows. A gel was considered to be formed when the resulting semi-solid would remain at the bottom, after the bottle was held in an inverted position for a period of at least 5 minutes without said mixture creeping or allowing the liquid phase to exude or drain off.

When such a condition was reached, the percentage of solid material in the gel was measured to determine the effectiveness of said material as thickener. It is understood that the less solid material required to establish gelation in a liquid propellant, the more efficient is that material.

The data listed in Table I illustrate the results obtained when several commercially available thickening agents were incorporated into the Ucon-type propellants identified respectively as U-11, 12, and 114. As seen from the tabulated figures, the best results were obtained using Cab-O-Sil (>99% SiO₂, fumed amorphous silica; particle size 0.011 μ), which required only about 6 parts by weight to gel the propellant. It should be remembered in selecting any gel propellant composition that several factors have to be considered. Notably the propellant and thickening agent should not form a reactive mixture, further the structural requirements of the aerosol container dictate the type of propellant and the quantity which may be used.

From a purely weight consideration, it has been found that the materials listed in Table II constitute the preferred embodiments of the thickening agent.

Table III lists the materials employed as thickening agents and their physical characteristics.

Table I.—Thickening agents

Solid	Wt. percent of solid needed to form a stable gel		
	U-11	U-12	U-114
Permangel.....	44	44	46
No. 219 Silica.....	52	49	53
Activated Carbon.....	21	21	20
Thixcin R.....	16	21	32
Ben-A-Gel.....	36	33	34
2151, Polishing Earth.....	17	18	18
No. 230 Rottenstone.....	48	47	54
No. 5 Talc.....	53	55	54
No. 399 Low Micron Mg Silicate.....	27	24	25
No. 155 Micalite.....	45	43	46
No. 295 White Rouge.....	38	37	42
Pumice No. 841 FFFF.....	42	42	45
No. 49 Bentonite.....	55	49	53
No. 85 Tripoli.....	48	46	48
Cab-O-Sil.....	6	4	6
Superfloss.....	16	14	17
Snowfloss.....	12	12	12
Attasorb L.V.M.....	19	19	18
Silica No. 22.....	45	41	48

Table II.—Preferred thickening agents

Solid	Wt. percent of solid needed to form a stable gel		
	U-11	U-12	U-114
Cab-O-Sil*	6	4	6
Snowfloss*	12	12	12
Superfloss*	16	14	17
2151 Polishing Earth.....	17	18	18
Attasorb L.V.M.....	19	19	18
Thixcin R.....	16	21	32

*Most preferred solids.

Table III.—Characterization of solids

Permangel—a colloidal, amorphous, highly purified attapulpus clay; about 66% SiO₂ on a volatile-free basis.
No. 219 Silica—about 99.75% SiO₂, crystalline; particle size, 98.5% through 325 mesh.
Activated Carbon—specially treated carbon having a high surface area; average particle size, 90% through 200 mesh screen.
Thixcin R—finely divided colloidal silica; particle size, 500 to 10³ millimicrons.
Ben-A-Gel—highly purified bentonite, composed principally of aluminum silicates; particle size, 100% through 200 mesh.
No. 2151 Polishing Earth—about 86% SiO₂, 5% Al₂O₃; particle size, 5 μ or less.
No. 230 Rottenstone—61% SiO₂, 18% Al₂O₃; 99.5% passes through 200 mesh screen.
No. 5 Talc—42% SiO₂, 23% MgO; 99.88% passes through 325 mesh screen.
No. 399 Low Micron Mg Silicate—51% SiO₂, 29% MgO; 100% passes through 325 mesh screen.
No. 155 Micalite—56% SiO₂, 28 % Al₂O₃; 99.3% passes through 325 mesh screen.
No. 295 White Rouge—about 96% SiO₂; particle size, 100% through 200 mesh.
Pumice No. 841 FFFF—about 70% SiO₂; 97% passes through 325 mesh screen.
No. 49 Bentonite—64% SiO₂, 21% Al₂O₃; 85–90% passes through 200 mesh screen.
No. 85 Tripoli—same as rottenstone; siliceous material resulting from the natural decomposition of siliceous standstone; particle size, 100% through 200 mesh.
Cab-O-Sil—>99% SiO₂; fumed amorphous silica; particle size, .011 μ .
Superfloss—calcined hydrated amorphous silica; particle size, 5 μ or less.
Snowfloss—hydrated amorphous silica, particle size, 5 μ or less.
Attasorb L.V.M.—hydrated Mg, Al silicate; heat treated to remove any volatile matter; 67% SiO₂, 13% Al₂O₃; particle size, 5 μ or less.
Silica No. 22—99.5% amorphous silica; 92–95% passes through 325 mesh.

From the foregoing description it may be seen that many advantages are obtainable in aerosol systems embodying the present invention. Commercial applications which heretofore could not utilize available powder sprays may readily adapt the disclosed propellant system and be assured of a substantially liquid-free spray of the material being dispensed.

It should be understood that in the practice of the disclosed propellant system many changes and modifications might be made by one skilled in the art without departing from the spirit and scope of the invention. For example, while the foregoing description has been directed primarily to a system for dispensing a dry powder stream, the propellant may also be utilized effectively to discharge other fluidized streams, such as an atomized liquid spray.

We claim:

1. A gelled propellant composition charge for aerosol-type dispensers, which composition consists essentially of: a vaporizable liquid fluorocarbon propellant characterized by a Trouton number not exceeding about 21.0, and a thickening agent selected from the group consisting of a silica-containing inorganic gelling agent and activated carbon, said thickening agent having a particle size less than about 10^3 microns, said thickening agent being present in the composition in an amount of at least 4 weight percent.

2. A gelled propellant composition charge for an aerosol-type container adapted to deliver a dry powder spray in a liquid-free stream of the propellant gas, which consists essentially of: a vaporizable liquid fluorocarbon propellant having a Trouton number not exceeding 21.0, and a silica-containing inorganic gelling agent in powder form and having a particle size no greater than about 44 microns, said agent being present in the composition in an amount of at least 4 to about 55 weight percent of the composition.

3. The gelled propellant composition of claim 2 wherein the gelling agent consists of a powdered material having a particle size between about 1 and 100 millimicrons.

4. A gelled propellant composition for aerosol containers consisting of a vaporizable liquid propellant selected from the group consisting of: trichloromonofluoromethane, dichlorodifluoromethane, monochlorodifluoromethane and dichlorotetrafluoroethane, and a silica-containing

inorganic gelling agent having a particle size no greater than 5 microns and in an amount of at least 4 weight percent, said agent being homogeneously intermixed with the vaporizable propellant gas to form a mass therewith having a gelled consistency.

5. The gelled composition of claim 4 wherein the gelling agent consists of a siliceous material containing amorphous silica component in an amount of at least 95 percent by weight of the agent, said agent having a particle size between about 1 and 100 millimicrons; said agent being present in the composition in an amount between 4 and 55 weight percent.

6. A gelled propellant composition for aerosol systems consisting essentially of a vaporizable fluorocarbon propellant characterized by a Trouton number not exceeding about 21.0 and at least 4 weight percent of the composition of a silica-containing inorganic gelling agent containing at least about 95 percent by weight amorphous silica and having a particle size less than about 44 microns.

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JULIUS GREENWALD, *Primary Examiner*.