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2,982,743

PRESSURIZED DECORATIVE SPRAY-PACKAGE

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No Drawing. Filed Feb. 1, 1960, Ser. No. 5,590

4 Claims. (Cl. 260-18)

This invention relates to a pressurized package to be used for the production of decorative sprays such as the so-called "artificial snows" which have become popular over the past few years.

Originally the "snow" formulations comprised a solution of a plastic resin which could be expelled from a valved pressurized container by a liquefied, normally gaseous propellant. Later a part of the resin was replaced by a normally solid, fatty acid such as stearic acid. Such compositions are described and claimed in United States Patents 2,659,704; 2,716,637; 2,803,906 and 2,835,997. The present invention comprises an improvement in formulations intended for production of decorative sprays of this character.

The package comprises a suitable container capable of withstanding the pressure of the propellant employed. These are well known in the so-called "Aerosol" industry. Among the most common are the so-called "beer can" containers of about 6-16 ounce capacity in which a variety of pressurized "self-spraying" formulations are sold including insecticides, deodorants, waxes, simulated or artificial snow, etc., etc.

The container is equipped with a quick acting valve of the type which will cause the formulation to be ejected as a "wet" spray when the valve is actuated. The formulation is broken up into small droplets which are deposited on the target. This is in contrast with the types of valves producing a space-spray which comprises a mist or fog; or the type producing a foam; or still another type producing a jet stream. There are a number of commercially available valves suitable for use in this invention, and they need not be described in detail. Usually they are equipped with a dip tube which extends to the bottom, or near the bottom of the container. The pressure of the propellant vapor in the container forces the liquid contents through the dip tube and out of the nozzle of the valve from which it emerges as a wet spray and is deposited on the target being decorated.

The container is usually filled to about 85-95% of its volume with a liquid formulation of this invention, although this may vary considerably one way or the other. Methods of filling such containers are well known and need not be described in detail.

The formulation of this invention consists essentially of (1) a propellant which is gaseous under normal temperature and pressure conditions; (2) a normally solid, free, fatty acid having for example 12-18 carbon atoms per molecule; (3) a solvent for the fatty acid; and (4) a small amount of a polyalkylene oxide having a molecular weight in excess of 200,000, and preferably of about 500,000 or more, which serves to cause the fatty acid to assume the desired flake form when propelled against the target.

The propellants suitably comprise the normally gaseous fluorocarbons. These are polyhalogenated low molecular weight hydrocarbons in which at least one of the

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halogens is fluorine, and usually at least one is chlorine. They have the formula $C_nCl_XF_{Y(2n-1)}$ wherein n is a whole number from 1 to 3, X is chlorine or fluorine, and Y is chlorine, fluorine, bromine, iodine or hydrogen. Examples of these are trichloromonofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, dichloromonofluoromethane, difluoromonochloromethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, monochloropentafluoroethane, and chlorodifluoromethyl methane, which have boiling points ranging from about $-30^\circ C.$ to $50^\circ C.$

These are sold by duPont under the trademark "Freon" and by other manufacturers under various other trademarks.

These propellants may be replaced in part by other propellants, for example, low boiling hydrocarbons, such as isobutane, normal butane, propane, etc. Such hydrocarbon propellants could be used by themselves except that they are flammable and hence may present a fire hazard. Consequently, the proportion of such hydrocarbon propellant is usually not more than about 10% of the total formulation.

The fatty acid should be solid at room temperature (e.g. about $70-85^\circ F.$) and may suitably comprise 12-18 carbon atoms. Higher molecular weight acids may be used provided they are sufficiently soluble. Suitable acids are stearic, palmitic, myristic, ricinoleic, etc., or mixtures thereof. Many commercial acids are mixtures in which one or another acid predominates, and such mixed acids are satisfactory provided they produce no odor problem. The preferred acids are saturated, since unsaturated acids may become rancid. From price considerations, as well as performance, stearic acid or mixtures in which it predominates, is preferred.

The solvent should be comparatively low boiling so that it will evaporate readily as soon as the formulation is sprayed. The fatty acid should be readily soluble in the solvent at relatively low temperatures, say $40-60^\circ F.$ to which the packages may sometimes be subjected. It should also be miscible with the propellant. The solvent, or at least the combination of solvent and propellant should also be capable of dissolving the resin and keeping it in solution at all temperatures likely to be encountered, or at least in the range of about $40-60^\circ F.$ and above.

Suitable solvents comprise methylene chloride, methyl chloroform, chloroform and other relatively low boiling chlorinated hydrocarbons. Trichlorofluoromethane or other non-propellant chlorofluoro hydrocarbons may be used provided the acid is sufficiently soluble therein. Mixtures of solvents may be used. Any organic solvent which is readily volatile at room temperature may be employed. From a practical standpoint, solvents presenting odor or fire hazard problems, or which are highly toxic should not be used, nor should those having vapor pressures so low that they do not evaporate readily.

The resin component is a high molecular weight polyalkylene oxide such as polyethylene oxide, polypropylene oxide, polybutylene oxide and the like. It should have a molecular weight preferably of about 500,000 to about 5,000,000 or more. It must be soluble in the solvent-propellant mixture. Polyethylene oxide is preferred, both because of its commercial availability and its excellent performance in exceedingly small proportions.

In addition to these ingredients, the formulation may comprise other additives such as perfumes, soluble dyes, etc., which enhance or impart a desired property to the composition, but which do not affect its essential characteristics.

The following indicates suitable ranges of proportions

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for the various components based on the total composition:

	Range	Preferred
Polyalkylene oxide (p.p.m.) ¹	100-2,500	100-2,000
Fatty Acid.....percent.....	5-25	5-20
Solvent.....do.....	30-50	35-45
Propellant.....do.....	Remainder	35-45

¹ Based on total composition. Amount used depends on molecular weight of the resin and the proportion of fatty acid employed.

The following comprise specific examples of suitable compositions. A base composition was made up as follows:

	Percent by weight
Stearic acid (double pressed)	16
Methylene chloride	44
Difluorodichloromethane	40

These components formed into a solution and charged to a suitable valved container cannot be dispensed to form a suitable decorative spray-coating, but rather resembles sprayed talcum powder.

When a suitable polyethylene oxide is dissolved in the formulation the dispensed spray is deposited in flake-like particles on the target forming an excellent simulated snow decoration.

The following table shows suitable proportions of polyethylene oxide polymers of varying molecular weight.

Formula	Tradename ¹	Approximate Mol. Wt.	Proportions Added To Base Formula, p.p.m.
1.....	Polyox Coagulant.....	5,000,000	150 (100-300)
2.....	Polyox WSR 301.....	3,500,000	~300 (200-600)
3.....	2,000,000	950-1,250
4.....	Polyox WSR 205.....	500,000	1,250-1,550
5.....	Polyox WSR 35.....	200,000	35,000 (3.5%)

¹ Trademark Carbide & Carbon Chemical Co.

There is a relationship between the molecular weight of the polyalkylene oxide and the proportions in which it is effective in producing a desirable flake structure of the sprayed composition. Thus, if a polyalkylene oxide of a molecular weight substantially below 500,000 is used, the amount of resin needed is quite high. At molecular weights of 500,000 or above the proportion of the polyalkylene oxide is surprisingly low, being less than about 0.25% by weight of the total composition, and usually below about 0.15 to about 0.2%. For this reason the lower molecular weight polyalkylene oxides are not equivalent to those of about 500,000 or more.

The polyalkylene oxides have unique characteristics. Six to eight times as much of a polyvinyl acetate resin of 2,000,000 molecular weight is required as for a polyethylene oxide of corresponding molecular weight. Other high molecular weight resins (e.g. 1.5-2.5 million) such as polyacrylates and methacrylates must be used in large amounts, or must be used together with 1-4% of another plastic resin of considerably lower molecular weight (e.g. polyvinylacetate, 90,000 m.w.). Thus, the advantages of the polyalkylene oxides used in this invention are readily apparent.

The proportion of polyalkylene oxide used depends not only on the molecular weight, but also on the proportion of acid used in the base formulation. Thus, when the Polyox coagulant of Formula 1 is used with the base formula containing 16% stearic acid, about 100-250 p.p.m. may be employed. If more than about 300 p.p.m. of this Polyox is used, the spray resembles coconut shreds or spaghetti rings. If omitted entirely, the acid is dispensed as a powder.

If the acid proportion is reduced, for example, to about 8%, the amount of Polyox is reduced proportionately.

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If the acid content is increased, the Polyox can be increased proportionately.

There is, however, a limit to the proportion of acid which can be employed, this being based upon the solubility of the acid in the solvent-propellant at both the dispensing temperature and a temperature somewhat lower, e.g. 40-60° F., since the package may sometimes be stored at such lower temperatures and separation of the solids is undesirable.

The proportions of solvent and propellant may vary. Since the propellant is usually the most expensive component of the composition, it is desirable to keep it as low as possible and still obtain the desired dispensing effect. This depends upon the vapor pressure of the particular propellant and its partial pressure in the mixture. This in turn is affected by the vapor pressure effect of the solvent. The absolute package pressure can be governed to some extent by the proportions of solvent and propellant, or by the use of more than one propellant and/or solvent.

The amount of a given solvent may also be limited by characteristics of the package parts, particularly valve seal rubbers. This is, of course, a matter of practical consideration, not directly related to this invention. In the base formula given above, a substantial increase in methylene chloride proportion would result in some rubber deterioration. As more resistant rubbers become available this factor becomes less critical.

The polyalkylene oxides may be polymers of ethylene oxide, propylene oxide, or butylene oxide, etc., polyethylene oxide being preferred.

The formulations of this invention have advantages over these heretofore used. They are more readily cleaned from draperies, furniture, windows, etc. than earlier formulations because the solids deposited consist almost entirely of the organic acid which is readily washed off with water and a detergent such as soap, ammonia, etc. Moreover, the polyalkylene oxides are largely water soluble, and are present in such low proportions as to have little effect on cleaning even if they were not. Earlier compositions containing higher percentages of plastics, many of which were not water soluble, were difficult to remove from the target. For example, earlier formulations contained resin to acid in ratios of 1:4 to 1:1 parts or higher. In the present invention the ratio of polyalkylene oxide to acid is in the range of about 1:500-1600 parts by weight.

The inclusion of small amounts of the polyalkylene oxides in the compositions of the character dealt with here and containing other plastic resins (as well as solid fatty acids), permits substantial reduction in the amount of such other resins and provides increased performance characteristics to the resultant compositions.

The examples given are for purposes of illustration and should not be construed as limiting the invention unduly. We claim as our invention:

1. In a pressurized self-spraying decorative spray composition comprising a normally solid free fatty acid such as those containing 12-18 carbon atoms per molecule, a solvent for said acid, and a liquefied normally gaseous propellant, the improvement which comprises incorporating in the composition about 100 to about 2500 p.p.m. of a polyalkylene oxide having from two to four carbon atoms in the monomer unit, and a molecular weight above about 200,000, based on the total formulation.

2. In a pressurized self-spraying decorative spray composition comprising a normally solid free fatty acid such as those containing 12-18 carbon atoms per molecule, a solvent for said acid, and a liquefied normally gaseous propellant, the improvement which comprises incorporating in the composition about 100 to about 2500 p.p.m. of a polyethylene oxide having a molecular weight above about 200,000.

3. The composition of claim 2 wherein the polyethylene oxide has a molecular weight of about 500,000 to about

5,000,000 and the weight ratio of polymer to acid is in the range of about 1:500-1600.

4. A pressurized self-spraying decorative spray composition comprising about 5% to 25% of a normally solid free fatty acid having from about 12 to about 18 carbon atoms per molecule, about 30% to about 50% solvent for said acid, about 100 to about 250 p.p.m. of polyethylene oxide, having a molecular weight above 500,000, the remainder consisting essentially of a liquified normally gaseous propellant.

References Cited in the file of this patent

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