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3,419,658 NONAQUEOUS AERÓSOL FOAMS CONTAINING MINERAL OIL

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ABSTRACT OF THE DISCLOSURE

An aerosol foam composition consisting essentially of: (a) White mineral oil,

(b) From 1 to 10% by weight of at least one surfactant having the structure RO(CH2CH2O)nH wherein R 15 is an aliphatic hydrocarbon radical selected from the group consisting of (1) saturated alkyl radicals of from 12 to 18 carbon atoms and (2) nonsaturated alkenyl radicals of from 12 to 18 carbon atoms, n is from 0 to 20;

(c) From 5 to 50% by weight of an aerosol propellent selected from the group consisting of hydrocarbons and chlorofluorohydrocarbons, said propellent having a boiling point between -50° C. and $+15^{\circ}$ C.

The present invention is directed to novel mineral oil aerosol foam compositions. In particular, this invention is concerned with compositions of mineral oils, certain specified surfactants and aerosol propellents which foam 30 when discharged from aerosol containers.

Production of foams by discharge from aerosol containers is well known. For example, U.S. Patent 2,655,480 discloses a number of aqueous systems and Canadian Patent 678,079 discloses a number of nonaqueous sys- 35 tems based on polyols. Prior to the present invention, foam producing compositions based on mineral oils have not been described. Such compositions would have many valuable uses as hereinafter described.

It is, therefore, an object of the present invention to 40 provide, for the first time novel nonaqueous aerosol foams containing mineral oils.

These and other objects will be apparent in the present specification which follows.

More specifically, the present invention is directed to 45 novel aerosol foam compositions comprising white mineral oil, from 1% to 10% by weight of a surfactant of structure $RO(CH_2CH_2O)_nH$ wherein R is an aliphatic hydrocarbon group of 12-18 carbons chosen from saturated alkyl and nonsaturated alkenyl groups and n is 50 from 0 to 20, and from 5% to 50% by weight of an aerosol propellent chosen from hydrocarbon and chlorofluorohydrocarbon having boiling points of from -50° C. to 15° C.

is a 50/50 by weight mixture of cetyl and stearyl alcohols.

The novel mineral oil compositions herein described and claimed are useful alone where treatment with a mineral oil is desired, e.g., as baby oils, or as a base for topical or cosmetic products such as cleansing creams, 60 lubricating creams, cream rouges, deodorant creams, suntan creams, hormone creams, vitamin creams, brilliantines, hair pomades, hair creams and ointments. The necessary added ingredients are combined with the basic formulation before being applied for the indicated uses. 65 2

The compositions of this invention comprise three essential ingredients, (A) the mineral oil, (B) a surfactant, and (C) the propellent. Mineral oil is usually a white, i.e., highly purified, mineral oil. This is necessary since most intended uses involve application to the human epidermis. Useful mineral oils are commercially available in a wide variety of viscosities, i.e., Saybolt viscosities (100° F.) of 55-400. All such oils are useful because the choice of mineral oil depends primarily on the 10 final product desired, but has a limited effect on the ability to foam, except as the nature of the propellent is effected.

The useful surfactants are those of structure

RO(CH₂CH₂O)_nH

R may be either an alkyl group of 12-18 carbons or a monounsaturated alkenyl group of 12-18 carbons. In the surfactants, n may vary from 0 to about 20. The surfactants are thus hydrocarbon alcohols or ethoxylated products thereof. Both types are well known in the art and commercially available. While R may be any alkyl or alkenyl group of the type herein defined, the straight chain groups derived from fatty acids by reduction are preferred. Typical examples are lauryl, myristyl, cetyl, stearyl, and oleyl alcohols. The ethoxylated products where n=1-20 are prepared by reaction of these alcohols with ethylene oxide by well known procedures.

The nature of the surfactant has an effect on the nature of foam produced. In general, as the relative amount of the ethylene oxide (the value of n) increases in the surfactant, the relative stability of the foam decreases. Thus, if highly stable foams are desired, the alcohol surfactants containing no ethylene oxide are preferred. On the other hand, if immediate collapsing foams are desired, the surfactants containing relatively large amounts of ethylene oxide are preferred. Both types of foams are useful for a number of purposes. The stable foams are useful in cleansing creams and like applications while the rapidly collapsing foams are useful in medicinal applications, suntan creams and the like where application as a foam is desired, but a persistent foam is not.

Mixture of surfactants may be used. In particular, an equal weight mixture of cetyl and stearyl alcohol has been found to be particularly useful. Where stable foams are desired, this mixture is the preferred surfactant of this invention.

At least 1% by weight of the total composition of surfactant, oil and propellent must be surfactant if foams are to be obtained. As high as 10% surfactant has been used and larger amounts probably could be used, but there seems to be no advantage in so doing. For most purposes the preferred surfactant concentration is from to 6%.

The propellents used in this invention are chosen from A preferred embodiment is one wherein said surfactant 55 hydrocarbons and chlorofluorohydrocarbons for boiling points between -50° C. and $+15^{\circ}$ C. Since the mineral oils vary in viscosity the propellents must be varied in vapor pressure accordingly to produce the most efficient results. The higher the viscosity of the mixture, the greater vapor pressure is required to propel the foam material from the container. The hydrocarbon propellents include propane, butane and isobutane. The chlorofluorohydrocarbon propellents include dichlorodifluoromethane, dichlorotetrafluoroethane, 1,1,1-chlorodifluoroethane, 1,1difluoroethane, mixtures of dichlorodifluoromethane and 3

dichlorotetrafluoroethane, mixtures of dichlorodifluoromethane and trichlorofluoromethane, monochloropentafluoroethane, 1,1,1 - trifluoroethane, s-tetrafluoroethane, pentafluoroethane, 1-chloro-1,1,2,2-tetrafluoroethane, perfluorocyclobutane, perfluoropropane, chloroheptafluoropropane and heptafluoropropane. Mixtures of the above hydrocarbons and the chlorofluorohydrocarbons may also be used. In addition, small amounts of inert gases such as nitrous oxide or carbon dioxide may also be added if de-

The amount of propellent used naturally varies with 10 the actual system being produced. In general, less than 5% propellent will not produce useful results. As much as 50% propellent has been used particularly with the low vapor pressure propellents. More than 50% propellent could possibly be used but seems to serve no known useful purpose. The preferred propellents are dichlorodifluoromethane, mixtures of dichlorodifluoromethane and monofluorotrichloromethane, dichlorotetrafluoroethane, and mixtures of the same with dichlorodifluoromethane because of their lack of flammability. With few exceptions, the propellents are soluble in the mineral oil base. The surfactants are usually isoluble. The compositions are prepared by warming the mineral oil and surfactant together with agitation until the surfactant has dissolved. Depending on the type of equipment available, the oilsurfactant mixture may be either combined with a propellent, then added to an aerosol container followed by capping with a foam valve, or by adding the oil-surfactant mixture to the aerosol container, capping with the 30 foam valve and pressure adding the propellent.

The following representative examples illustrate the present invention.

EXAMPLE 1

This example illustrates the use of a variety of sur- 35 factants and the effect these have on the resulting foams.

and finally pressure loading the propellent in the indicated amount. All of these compositions contain 79% mineral oil of Saybolt viscosity 200-210 seconds, 6% surfactant and 15% CF₂Cl₂ propellent, all by weight. The

conditions and results obtained are shown in Table I. EXAMPLE 2

This example illustrates the effect of variations in the reactive amounts of cetyl and stearyl alcohols in mixtures there of used as surfactants. The procedure of Example 1 was followed, each of the compositions again containing 79% mineral oil, 6% surfactant and 15% CF₂Cl₂ propellent. The results are shown in Table II.

EXAMPLE 3

This example illustrates the effect of varying surfactant concentration. The compositions were prepared using the procedure of Example 1 at the surfactant concentrations indicated in Table III. The surfactant in each case is a 50/50 mixture by weight of cetyl and stearyl alcohols. The results are shown in Table III.

EXAMPLE 4

This example illustrates the effect that different propellents have on the results. The formulations, prepared by the method of Example 1, each contained 79% mineral oil, 3% cetyl alcohol, 3% stearyl alcohol and 15% propellent by weight. The results are shown in Table IV.

EXAMPLE 5

This example illustrates the effect of changes in propellent concentration. The formulations, prepared by the method of Example 1, each contain 3% cetyl alcohol, and 3% stearyl alcohol by weight as surfactants. The variation in propellent concentration on the results obtained are shown in Table V.

TABLE I

Surfactant ¹	Appearance of Aerosol	Type of Foam
"Polawax" (ethoxylated stearyl alcohol)		
"Brij" 30 C ₁₂ H ₂₅ O(CH ₃ CH ₂ O) ₄ H	Clear	Do
"Brij" 52 C ₁₆ H ₃₃ O(CH ₂ CH ₂ O) ₂ H	do	mediately.
"Brij" 56 C ₁₆ H ₃₃ O(CH ₂ CH ₂ O) ₁₀ H	Good dispersion of solid	Foam collapses immediately after discharge.
"Brii" 58 C16H33O(CH9CH9O)96H	do	Do.
"Brij" 58 C ₁₆ H ₃₃ O(CH ₂ CH ₂ O) ₂₀ H "Brij" 72 C ₁₈ H ₃₇ O(CH ₂ CH ₂ O) ₂ H	Clear	Typical large bubble size, stable foam.
"Brij" 76 C18H37O(CH2CH2O)10H	Good dispersion of solid	Large bubble size that collapses slowly.
"Brij" 78 C18H3; O(CH2CH2O)20H		Collapses immediately.
	cakes on bottom.	
"Brij" 92 oleyl O(CH2CH2O)2H	Clear	Do.
"Brij" 96 oleyl O(CH2CH2O)10H	Liquid dispersion	Do.
"Brij" 98 oleyl O(CH2CH2O)20H		Do.
Cetyl alcohol/stearyl alcohol (50/50)		
"Lorol" 34 (Cetyl alcohol)2		
"Siponic" E-0 (ethoxylated stearyl cetyl alcohol, 1- ethylene oxide unit).		Very large bubble size, stable.
"Siponic" E-1 (ethoxylated stearyl-cetyl alcohol, 2 ethylene oxide units).		Do.
Myristyl alcohol	Clear	Medium size bubble size foam that collapses within about 30 seconds.

^{1 &}quot;Brij" surfactants are marketed by Atlas Chemical Industries, Inc. "Siponie" surfactants are marketed by Alcolac Chemical Corporation. "Lorol" 24 cetyl alcohol and "Lorol" 28 stearyl alcohol are products of the Du Pont Company.

² Tested with high viscosity mineral oil (Saybolt viscosity 345-355).

The compositions were prepared by heating the liquid oils and surfactants together until solution occurred, cooling the solution, placing it in an aerosol container, sealing the container with a commercially available sealing valve

"Polywax" is a creamy, waxlike solid with a melting range of 48°-52° C., iodine value of 3.5 maximum and a saponification value of 9-14. (American Perfumer and Cosmetics, vol. 79, No. 3, March 1964, p. 56.)

TABLE II

Mineral Oil	Cetyl alcohol ratio/ Stearyl alcohol	Form of Dispersed Solid	Type of Foam
Saybolt Viscosity, 50-60 sec	100/0	Plates	
Do	75/25	Almost completely soluble	Very large bubble size, unstable
Do	50/50	Amorphous.	Large hubble size, unstable
Do	25/75	Plates	•
Do	0/100	do	
Saybolt Viscosity, 65–75 sec	100/0	do	
D0	75/25	Almost amorphous Amorphous	Very large hubble size unetable
Do	50/50	Amorphous	Large hubble size
Do	25/75		
Do	0/100	Plates	
Saybolt Viscosity, 80-90 sec	100/0	do	
Do	75/25	Amorphous and plates	Very large highble size
Do	50/50	Amorphous	Large hubble size
<u>D</u> o	25/75	More plates than amorphous	Zargo babbic bize.
Do	0/100	Plates	
Saybolt Viscosity, 95–105 secs	100/0	do	
D_0	75/25	Amorphous and plates	Do.
Do	50/50	Amorphous	Do
<u>D</u> 0	25/75	Mostly plates	20.
D ₀	0/100	Plates	
Saybolt Viscosity, 125-135 secs	100/0	do	
Do	75/25	Agglomerates	Do
Do	50/50	Amorphous	Dα
Do	25/75	WOSLIV DIALES	
Do	0/100	Plates	
Saybolt Viscosity, 180–190 secs	100/0	do	
D_0	75/25	Agglomerates	Do .
Do	50/50	AMOrphous	Do
Do	25/75	Mostly plates	Large highlie size unetable
Do	0/100		
Saybolt Viscosity, 200–210 secs	100/0	Good dispersion of plates	Large hubble size !
Do	75/25	Agglomerates	Do.
Do	50/50	Amorphous	Do.
Do	25/75	Mostly plates	Do.
Do	0/100	Plates	20.
Do Saybolt Viscosity, 345–355 secs	100/0	Plates (good dispersion)	Do.
D0	75/25	Some agglomerates	Do.
Do	50/50	Amorphous	Do
D_0	25/75	Mostly plates	Do. Do.
Do	0/100	Plates	Do.

 $^{{}^{\}rm I}$ These foams flashed over the surface after discharge and then collapsed.

TABLE III

	Composition	(Wt. per	cent)		
Surfactant Minera Type	Mineral oil			Appearance of Aerosol	Type of foam
	Type	Conc.	- CF ₂ Cl ₂	\mathfrak{I}_2	
1.0	Low viscosity 1	84.0	15.0	Clear	- No foam.
1.0	High viscosity 2	84.0	15.0	do	
2.0	Low viscosity	83.0	15.0	do	Large bubble size, very unstable.
	High viscosity	83.0	15.0	do	Large bubble size, collapsed im- mediately.
	Low viscosity	82.0	15.0	Few agglomerates present	Slight foam, unstable.
3.0]	High viscosity	82.0	15.0	Poor dispersion of solid	- Large bubble size foam.
1.0		81.0	15.0	Poor, many agglomerates	
.01	High viscosity	81.0	15.0	Good dispersion of solid	. Do.
	Low viscosity	80.0	15.0	Many agglomerates	_ Do.
	High viscosity	80.0	15.0	Good dispersion of solid	Do.
	Low viscosity	7 9. 0	15.0	do	
3.0]	High viscosity	79.0	15.0	do	. Do.

Low viscosity mineral oil Saybolt Viscosity, 50-60 seconds.
 High viscosity mineral oil Saybolt Viscosity, 345-355 seconds.

TABLE IV

		TABLE IV	
Propellent	Mineral oil	Appearance of Aerosol	Type of Foam
CH ₃ CF ₂ Cl. CH ₃ CF ₇ Cl CH ₃ CHF ₂ CH ₃ CHF ₂ Isobutane Do	High viscosity 2 Low viscosity High viscosity Low viscosity High viscosity Low viscosity High viscosity Low viscosity High viscosity Low viscosity Low viscosity Low viscosity Low viscosity Low viscosity Low viscosity Low viscosity Low viscosity	dodododododododo.	Do. Do. Do. Do. No foam, insufficient pressure. Large bubble size. Very large bubble size. Very large bubble size. Very large bubble size. Large bubble size. Large bubble size. Rough surface foam. Large bubble size. Do.

¹ Low viscosity mineral oil=Saybolt viscosity 50-60 seconds.
² High viscosity mineral oil=Saybolt viscosity 350 seconds.

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No.	Mineral Oil	Composition, Wt. Percent CF ₂ Cl ₂ Propellent		
1	1 89	5.0	5	
2	1 84	10.0	U	
3	1 79	15. 0		
4	1 74	20.0		
5	1 69	25.0		
6	1 44	50.0		
7	2 89	5. 0		
8	2 84	10.0		
9	2 79	15.0	10	
10	2 74	20. 0		
	² 69	25. 0		
11	2 44	50.0		
14	- 11	50.0		

t Low Viscosity oil, Saybolt Viscosity 50-60 secs.
² High Viscosity oil, Saybolt Viscosity 345-355 secs.

Appearance of aerosol

All of the products have good dispersions of the solids. The viscosity decreases as the propellent concentration increases. Formulation No. 1 is fairly fluid while Formulation No. 7 is almost a gel. Formulation No. 2 and Formulation No. 8 are fairly fluid.

Type of foam

Formulation No. 1 does not produce a foam due to insufficient pressure. Formulation No. 7 gives a low foam. 25 The formulations with 15% and 20% propellent give very pressure-sensitive foams while those with 25% and 50% propellent give much more coherent and less pressure-sensitive foams.

The preceding representative examples may be varied 30 within the scope of the present total specification disclosure as understood and practiced by one skilled in the art to achieve essentially the same results.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are as follows.

I claim:

1. An aerosol foam composition consisting essentially of:

(a) white mineral oil,

- (b) from 1 to 10% by weight of at least one surfactant having the structure RO(CH₂CH₂O)_nH wherein R is an aliphatic group selected from the group consisting of (1) alkyl of from 12 to 18 carbon atoms and (2) alkenyl of from 12 to 18 carbon atoms, n is from 0 to 20; and
- (c) from 5 to 50% by weight of an aerosol propellant selected from the group consisting of hydrocarbons and chlorofluorohydrocarbons, said propellant having a boiling point between 50° C. and +15° C.
- 2. An aerosol foam composition according to claim 1 wherein said surfactant is a mixture of cetyl and stearyl alcohols.
- 3. An aerosol foam composition according to claim 1 wherein said surfactant is a 50/50 by weight mixture of cetyl and stearyl alcohols.

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ALBERT T. MEYERS, Primary Examiner.
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U.S. Cl. X.R.

252-90, 305; 424-47

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,419,658

December 31, 1968

Paul Amsdon Sanders

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 16, "50° C." should read -- -50° C. --.
Signed and sealed this 17th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR. Commissioner of Patents