United States Patent Office 2,978,415 Patented Apr. 4, 1961

2,978,415

GUANIDINE SOAPS AS DRY CLEANING DETERGENTS

Ralph J. Chamberlain, Stamford, Conn., assignor to American Cyanamid Company, New York, N.Y., a corporation of Maine

No Drawing. Filed Apr. 17, 1957, Ser. No. 653,277
4 Claims. (Cl. 252—118)

This invention relates to a class of guanidine soaps of unsaturated higher fatty acid mixtures which are particularly well suited for use as detergents in dry cleaning solvents. The invention includes the washing or dry cleaning of soiled fabrics in organic solvents containing these guanidine soaps as well as the soaps themselves, which are believed to be new compositions, and methods for their preparation.

Dry cleaning consists essentially in agitating soiled garments, cloth or other textiles in a dry cleaning solvent having solvent power for the grease or other soil to be removed. Typical solvents that have been used commercially for this purpose include chlorinated aliphatic hydrocarbons such as perchlorethylene, trichlorethylene, carbon tetrachloride and mixtures of carbon tetrachloride (70 mole percent) with ethylene dichloride (30 mole percent). The most widely used solvents are petroleum hydrocarbon fractions including particularly Stoddard solvent which is a petroleum distillate having a minimum flash point of 100° F. and a volatility such that not less than 50% is recovered by 350° F., not less than 90% by 375° F., and an end point of about 410° F. when a sample is distilled. Another petroleum solvent in common use is 140–F solvent, which is a petroleum distillate similar to Stoddard solvent but with a minimum flash point of 140° F.

Soap detergents are commonly used in the above and similar dry cleaning solvents to facilitate the removal of soil from the fabrics being washed. Alkali metal soaps and amine soaps of oleic acid are most commonly used for this purpose. The concentration of soap in the dry cleaning solvent may vary widely with the type of soap used and with the nature of the textiles to be cleaned, but is usually within the range of about 1 lb. for each 6–35 gallons of solvent.

Commercial dry cleaning processes are frequently carried out in a perforated horizontal cylinder rotating inside a metal shell and known as a washer. Sufficient solvent is run into the washer so that the cylinder is filled to a depth of approximately ¼ to ⅓ of its diameter and the textiles to be dry cleaned are then placed in the cylinder. In cleaning wool the quantity of solvent is usually about 1 gallon for each pound of fabric; with cotton and rayon fabrics the proportion is slightly less. The washer is connected to a filter so that the solvent can be continuously freed from suspended impurities during the rinsing operation. The detergent is usually added to the washer after the cloth has been wet out in the dry cleaning solvent; in some cases a small amount of water is also added. The washer is then turned without circulation of the solvent through the filter for some 15–40 minutes or until the fabrics are cleaned, after which the filter circulation is begun to rinse the soil and the detergent from the textiles. The textiles are then centrifuged to remove excess solvent and are dried in a current of hot gases.

My present invention is based on the discovery that the guanidine soaps of higher fatty acids containing both oleic acid and linoleic acid are excellent dry cleaning detergents. In particular, I have found that the soaps prepared by neutralizing higher fatty acid mixtures containing approximately equal percentages of oleic acid and linoleic acid with guanidine or guanidine salts exhibit a number of advantageous properties when used in dry cleaning processes. They posses excellent detergency in dry cleaning solvents and also exhibit a low degree of soil redeposition; that is, they maintain the grease and dirt suspended in the organic solvent so that it is not redeposited on the fabrics. In addition, these new soaps possess good antistatic properties and small amounts retained by the cloth therefore assist in preventing the accumulation of dust and lint on the dry cleaned fabrics or garments.

Guanidine soaps falling within the scope of my invention may be prepared from a number of fatty acid mixtures that are available commercially, or that can be prepared from commercial fatty acid mixtures by simple refining processes. In general the fatty acid mixture should have a relatively high content, preferably within the range of about 30–60% by weight, of both oleic and linoleic acids and a comparatively low content of saturated fatty acids, which are undesirable in dry cleaning soaps. While a number of naturally occurring fatty acid mixtures such as soya bean oil fatty acids, sesame seed oil fatty acids and the like may be used, the preferred raw materials are the tall oil fatty acids, which are obtainable commercially in large quantities. These acids are produced by the vacuum steam distillation and fractionation of tall oil, a mixture of unsaturated fatty acids and rosin acids obtained as a by-product in the digestion of pine chips by the Kraft or sulfate process. The distilled acid mixtures of commerce usually contain about 90–97% of total fatty acids of which about 50% is oleic acid and 46–48% is linoleic acid.

My new guanidine soaps are preferably prepared by reacting one or more of these fatty acid mixtures with guanidine carbonate or with a guanidine salt of a stronger acid, such as guanidine hydrochloride, in the presence of an acid acceptor such as sodium carbonate or sodium hydroxide. Typical manufacturing processes are described in the following examples. The resulting soaps usually contain less than 5% of free fatty acid and are soluble in all proportions in polar organic solvents such as ethanol and isopropanol. They are also soluble in xylene, perchlorethylene and other chlorinated dry cleaning solvents. By the use of cosolvents such as isopropyl alcohol, isopropyl acetate or ethylene glycol monobutyl ether they can readily be dissolved in Stoddard solvent or other similar petroleum hydrocarbon solvents to the concentrations ordinarily used in dry cleaning which, as noted above, are usually on the order of about 1 lb. of the guanidine soap for each 6–35 gallons of solvent.

It will be understood from the foregoing that the essential feature of my dry cleaning method is the washing of fabrics in a dry cleaning solvent containing detergent quantities of a guanidine soap of a fatty acid mixture having a substantial content of both oleic acid and linoleic acid and a relatively low content, preferably not more than about 15%, of saturated fatty acids. The term, detergent quantities, as used in the present specification and claims, designates quantities of the guanidine soap sufficient to impart detergency and facilitate the removal of soil from the fabrics being washed. Stated numerically, these quantities are usually within the range of about 1 lb. for each 6 to 35 gallons of dry cleaning solvent, and preferably about 1 lb. for each 10–25 gallons. The process is not restricted to the use of any particular organic dry cleaning solvent or solvent mixture and any known or approved dry cleaning solvent, including particularly those enumerated above, may be used.

The guanidine soaps of my invention may be used in the quantities indicated above as the only detergent or they may be replaced in part by other detergents such as potassium or sodium oleate soaps, amine oleate soaps

or other accepted dry cleaning detergents. It is an advantage of the guanidine oleate-linoleate soaps of my invention that they are compatible in dry cleaning solvents with these soaps and with anionic wetting agents such as sodium dioctyl sulfosuccinate, sodium dihexyl sulfosuccinate, sodium lauryl sulfate, salts of alkylated aromatic sulfonic acids such as keryl benzene sulfonate and alkali metal salts of the sulfonic acids of condensation products of butylene and propylene polymers of about 12 carbon atoms with benzene or toluene. They are also compatible in dry cleaning solvents with nonionic surface active agents such as ethylene oxide or propylene oxide condensation products of alkylated phenols; a typical compound of this class is the condensation product of 8–9 moles of ethylene oxide with one mole of nonyl phenol that is sold commercially as "Aerosol NI." These and other wetting agents of the same class may therefore be present during the dry cleaning method of my invention, preferably in quantities of about 0.05% to 1% on the weight of the solvent. Other customary or preferred ingredients may also be present such as finely divided diatomaceous earth or other filter aids, which are usually employed in quantities of about 1–3%.

The invention will be further described and illustrated by the following specific examples. It will be understood, however, that although these examples may describe in detail certain preferred embodiments of the invention, including particularly the preferred guanidine soaps of tall oil fatty acid mixtures and their methods of manufacture, the examples are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

EXAMPLE 1

The guanidine soaps used in the tests of Example 2 were prepared by the following procedures.

In making the oleate-linoleate soap a commercial fatty acid mixture sold as "Acintol FA–2" was used. This mixture has an acid number of 194, a saponification number of 196 and contains 96.8% of fatty acids of 18 carbon atoms, 1% rosin acids and 2.2% unsaponifiables. The fatty acids consist of 50% oleic acid, 48% linoleic acid and 2% saturated acid.

A portion of this mixture weighing 768 grams was dissolved in 1050 cc. of methyl isobutyl ketone in a reaction vessel equipped with a condenser and stirrer and 259 grams of guanidine carbonate was added slowly during 30 minutes. The solution was stirred for an additional hour and was then tray-dried to constant weight in a forced-draft oven. The yield was 911 grams, which is 98% of theory. The dried product was a brown-colored stiff paste.

The same product can be prepared from other guanidine salts such as the nitrate, sulfate, hydrochloride and the like by the use of an acid acceptor such as sodium hydroxide or carbonate. The following preparation from guanidine hydrochloride is typical.

	Lbs.
"Acintol FA–2"	3,105
Guanidine hydrochloride	1,024
Toluene	385
Isopropyl alcohol	128
Sodium hydroxide, 50% aq. soln.	856

The fatty acid, guanidine hydrochloride and solvents are charged into a closed reaction kettle equipped with heating coils, an agitator and a condenser and heated to 80° C. and the sodium hydroxide solution is added slowly. The reaction is exothermic and refluxing occurs during the last part of the alkali addition. Water is then removed by azeotropic distillation, the organic solvent being returned to the kettle. When the dehydration is complete the batch is filtered hot (above 85° C.) to remove sodium chloride and the filtrate is stripped of solvents by distillation under a vacuum such as to attain a final temperature of about 100° C.

Either of these methods can be used to prepare guanidine soaps from other oleic-linoleic acid mixtures. A wide variety of natural or synthetic commercial fatty acids containing predominant amounts of such mixtures are available and may be used. The following fatty acid mixtures are typical of those included within the invention in its broader scope; the analyses of the seed oils are taken from Hilditch "The Chemical Constitution of Natural Fats" (1941), the figures being percent by weight.

	Oleic	Linoleic	Palmitic	Stearic
Soya Bean Oil	33.7	52.0	6.8	4.4
Sesame Seed Oil	49.4	37.7	7.8	4.7
Pine Seed Oil	35.1	54.5	----------	2.9
Tall Oil Fatty Acids[1]	50–51	46–48	----------	2–3

[1] Contains 1–4% rosin acids and 2–4% unsaponifiables.

The guanidine soaps of saturated fatty acids of 16 to 18 carbon atoms are not good dry cleaning detergents and therefore fatty acid mixtures having a relatively low content of these acids, preferably not more than about 10–15%, should be selected. Commercial fatty acids which are otherwise suitable, such as cottonseed oil fatty acids, may be pretreated by low temperature crystallization or solvent extraction to remove part or all of their saturated fatty acid content and may then be converted into guanidine soaps by the above-described procedures. In general the fatty acid mixtures used in making satisfactory guanidine soap dry cleaning detergents should contain from about 30% to 60% by weight of oleic acid and about 30–60% of linoleic acid.

Guanidine coconutate was prepared by dissolving 636 grams of coconut oil fatty acids in 1 liter of methyl isobutyl ketone, heating the solution to 80°–90° C. and adding 283 grams of guanidine carbonate slowly followed by agitation at the same temperature for one hour and drying at 50° C.

EXAMPLE 2

Dry cleaning solutions having the following compositions and properties were prepared. In each case the solvent was 2 liters of perchlorethylene (tetrachlorethylene).

Table I

Solution No.	1	2	3
Detergent	Potassium Oleate	Guanidine Oleate-Linoleate	Guanidine Coconutate
Weight, grams	125 (20% Soln.).	20	20.
Appearance	Translucent white.	Pale Amber	Pale Amber.
Viscosity:			
Poises	0.32	0.32	1.76.
Ford Cup No. 3	18.0	20.0	50.2.

The potassium oleate was a standard dry cleaning soap (Textile Test Method CCC–T–1916, May 1951, Method 5580) prepared by pouring a solution of 35 grams of KOH in 89 ml. of distilled water into a mixture of 250 ml. of oleic acid, 724 ml. of Stoddard solvent and 105 ml. of cyclohexanol. The guanidine oleate-linoleate and guanidine coconutate were those prepared as described in Example 1.

Wool flannel cloth was padded to a 125% pickup in a mixture of the following:

Carbon black	grams	0.75
Lard	do	0.75
White mineral oil	do	300
Acetone	cc.	300
Carbon tetrachloride	cc.	700

It was then cut into 6 x 6-inch pieces and 200 gram samples of these were dry cleaned in the test solutions.

In order to measure the soil redeposition-inhibiting properties of the detergents additional 6 x 6-inch pieces of unsoiled wool and of viscose rayon were washed in admixture with samples of the soiled wool. Test pieces of these were removed 7.5, 15 and 25 minutes after starting the washer (a rotating jar) and also at the end of the wash (35 minutes). Each piece was rinsed in 40 cc. of fresh perchlorethylene and dried by centrifuging and its reflectance was measured. The test results are shown in Table II; in this table the heading "Soln. No." refers to the solutions described in Table I, and the percent of soil removed is calculated by the formula:

$$\frac{\text{Reflectance: washed fabric—soiled fabric}}{\text{Reflectance: unsoiled fabric—soiled fabric}} \times 100$$

Table II

Soln. No.	Fabric	Wash Time, Minutes	Reflectance at 600 mu.		Soil Removed, Percent	Reflectance Loss, Percent
			Measured	Average		
Control	Soiled Wool.	None		52.8		
Do	Unsoiled Wool.	None		70.4		
Do	Unsoiled Rayon.	None		82.5		
1	Soiled Wool.	35	68.9	69.2	93	
1	do	35	69.5			
1	do	35	69.3			
1	Unsoiled Wool.	7	68.5			1.9
1	do	15	69.2			1.2
1	do	25	69.4			1.0
1	do	35	69.4			1.0
1	Rayon	7	71.1			11.4
1	do	15	68.8			13.7
1	do	25	66.9			15.6
1	do	35	64.9			17.6
2	Soiled Wool.	35	69.7	69.8	97	
2	do	35	69.9			
2	do	35	69.7			
2	Unsoiled Wool.	7	69.9			0.5
2	do	15	69.9			0.5
2	do	25	70.4			0
2	do	35	70.3			0.1
2	Rayon	7	82.1			0.4
2	do	15	81.4			1.1
2	do	25	81.7			0.7
3	Soiled Wool.	35	43.9	44.0	−50	
3	do	35	44.5			
3	do	35	43.6			
3	Unsoiled Wool.	7	53.9			16.5
3	do	15	49.7			20.0
3	do	25	47.2			23.2
3	do	35	45.8			24.6
3	Rayon	7	81.6			0.9
3	do	15	80.5			2.0
3	do	25	80.8			1.7
3	do	35	79.2			3.3

These results show that the guanidine oleate-linoleate soap is superior to potassium oleate both in its dry cleaning detergency and in its soil redeposition properties for wool and that the latter properties are much better with respect to rayon. The guanidine salt of coconut fatty acids has very poor detergency in dry cleaning solvents.

What I claim is:

1. A dry cleaning method which comprises washing soiled fabrics in a dry cleaning solvent containing detergent quantities of the guanidine soap of a fatty acid mixture containing about 30–60% of oleic acid, about 30–60% of linoleic acid and not more than about 15% of saturated fatty acids.

2. A dry cleaning method which comprises washing soiled fabrics in a dry cleaning solvent containing detergent quantities of the guanidine soap of tall oil fatty acids produced by the vacuum steam distillation and fractionation of tall oil.

3. The guanidine soap of a fatty acid mixture suited for use as a detergent in dry cleaning solvents containing about 30–60% of oleic acid, about 30–60% of linoleic acid and not more than about 15% of saturated fatty acids.

4. The guanidine soap of a tall oil fatty acid mixture suited for use as a detergent in dry cleaning solvents of about 50% of oleic acid and 46–48% of linoleic acid, the balance being saturated fatty acids.

References Cited in the file of this patent

UNITED STATES PATENTS

1,830,970	Sullivan	Nov. 10, 1931
2,240,365	Dreger	Apr. 29, 1941
2,374,113	Lowe	Apr. 17, 1945
2,551,634	Price	May 8, 1951
2,695,250	Shields et al.	Nov. 23, 1954

OTHER REFERENCES

Ind. and Eng. Chem., February 1948, vol. 40, No. 2, pages 335–337.

Soap and San. Chem., June 1951, pages 43, 45, 47, 57.

Dugan: "Fatty Acid Composition of Food Fats and Oils," Am. Meat Institute Foundation, C36, August 1957, page 6.