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MINERAL OILS CONTAINING ALKOXYALKYLOLAMINE EPICHLORHYDRIN CONDENSATION PRODUCTS

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This invention relates to mineral oil compositions and more particularly to oils of this type which contain a cationic emulsifying agent capable of producing oil-in-water emulsions of fine particle size wherein the oil droplets are substantive to cellulose fibers such as paper fibers, cotton textiles and the like.

Emulsions of mineral oils of widely varying viscosities have previously been prepared for a number of purposes. Colorless light mineral oils of relatively low viscosity, such as those having Saybolt Universal viscosities of 30–60 seconds at 100° F., are emulsified in water and used for the oiling of acetate or cuprammonium rayon, and also for natural silk. Somewhat heavier oils, having viscosities within the range of 90–150 seconds, are used in the preparation of cosmetic creams. Still heavier refined white oils, with viscosities as high as 350 seconds or more, are used in emulsified form for a number of purposes including internal medicinal uses. Any of these mineral oils can be made self-emulsifiable in water by dissolving therein the novel emulsifying agents of the present invention.

In accordance with my present invention, self-emulsifying mineral oils are obtained by incorporating therein emulsifying quantities of a particular class of cationic emulsifying agents. These new emulsifying agents are prepared from higher aliphatic amines of 12–18 carbon atoms that have been reacted with ethylene oxide or propylene oxide, such as the ethoxyethylolamines obtained by condensing 1 mol of the higher aliphatic amines with from 2 to about 10 mols of ethylene oxide. Such condensation products have previously been suggested as emulsifying agents for mineral oils.

I have found that much better emulsifying properties for hydrocarbon oils are imparted to the amine-alkylene oxide condensation products when these products are condensed with small amounts of epichlorohydrin. Thus, for example, by reacting 1 mol of octadecylamine-ethylene oxide condensation products containing from 2 to about 10 mols of combined ethylene oxide with from 0.05 to 0.5 mols of epichlorhydrin, an excellent class of spontaneous emulsifiers is obtained for paraffinic hydrocarbon oils having viscosities of 80 seconds at 100° F. The ordinary octadecylamine ethylene oxide condensation products are not good emulsifying agents for this particular type of oil.

The commercial importance of my discovery is evident. Self-emulsifiable mineral oils are in wide commercial use in the manufacture of products composed of or containing felted cellulose fibers, as well as for textile softeners, textile lubricants and the like. When used for these purposes the condensation products of the present invention possess all the advantageous properties of a highly efficient oil-soluble cationic emulsifying agent including the production of aqueous emulsions of oil droplets which exhaust or absorb on cellulosic fibers in water suspension. The emulsified oils can therefore be applied to cellulosic paper fibers, in the beater or elsewhere in the stock system, before they are formed into paper; the emulsions can also

be applied to cotton threads, cotton cloth and to other cellulosic textiles.

Although any aliphatic primary amine of 12 to 18 carbon atoms may be used, octadecylamine is the preferred starting material. Octadecylamines are available commercially in several grades and any of these may be employed; their usefulness is not materially impaired by the presence of a small proportion of unsaturated amine. The condensation of ethylene oxide or propylene oxide with the amine is carried out most advantageously by diluting the amine with a polar solvent such as a propyl or butyl alcohol and passing in the alkylene oxide at atmospheric or slightly elevated pressures while maintaining the reaction mixture at the boiling point of the alcohol until the desired quantity has been chemically combined.

The condensation between the alkoxyalkylolamine and epichlorhydrin is carried out simply by heating the two ingredients together in the desired molar ratio. Theoretically one mol of epichlorhydrin can be reacted with one mol of amine; however, reaction products of from 0.05 to 0.5 mols of epichlorhydrin for each mol of amine are employed as those containing a larger proportion of combined epichlorhydrin have only a low solubility in hydrocarbon oils. Usually a satisfactory degree of condensation is obtained by heating the reagents together at about 60–80° C. for about 0.5 to 2 hours. The condensation product is soluble in xylene, in paraffinic hydrocarbon oils, and in other hydrocarbons, and can be used as a solution in any of these solvents.

The quantity of condensation product to be dissolved in mineral oil for the preparation of self-emulsifiable oil compositions will depend on the particular properties desired in the oil. As little as about 2.5%, based on the weight of the oil, is sufficient to produce an oil composition that will form a stable emulsion in water; however, for most purposes quantities of 5–10% are preferable. From this range the amount of condensation product may increase to as much as 30–40% by weight of the oil-alkoxyalkylolamine-epichlorhydrin condensation product composition, particularly where the oils are used to obtain improved softness and absorbency in paper.

The invention will be further illustrated by the following specific example. It should be understood, however, that while this example may describe in detail certain specific features of the invention, it is given also for illustration and the invention in its broader aspects is not limited thereto.

Example

A mixture of 61.7 lbs. of a commercial octadecylamine and 7.4 gallons of sec-butyl alcohol was charged to a glass lined kettle equipped with a brine-cooled condenser. These materials were heated to about 90° C. and ethylene oxide gas was passed into the kettle. After the reaction had started the materials were cooled so that the temperature was maintained at from 85° C.–100° C. After 11.5 hours the temperature of the reaction mixture was maintained at from 90° C.–100° C. for an additional 2 hours to insure complete reaction of the ethylene oxide. Thereafter the product was stripped of solvent and volatile materials by heating to 120° C. under a vacuum of 20–30 mm. Hg. The product contained 3.7 mols of combined ethylene oxide for each mol of octadecylamine and was an orange-brown liquid at room temperature; it contained 96.3% of active material.

To portions of the condensation product weighing 480 grams (1 mol) there were added quantities of epichlorhydrin varying from 4.63 grams (0.05 mol) to 46.25 grams (0.5 mol) and the mixtures were heated on an oil bath for 1 hour. The resulting products were limpid, slightly viscous red-brown liquids that were soluble in mineral oils.

These products were dissolved in a heavy mineral oil

having a viscosity of 79 seconds at 100° F. The oils were tested by pouring the oil into water at room temperature, stirring for 5 minutes, and allowing the emulsion to stand for 24 hours. In the headings of the following table "ratio" means the molar ratio of epichlorhydrin to ethoxyethyloctadecylamine; the "10% emulsion" contained 10 grams of mineral oil and 1 gram of emulsifier in 89 grams of water and the "5% emulsion" contained 5 grams of mineral oil and 0.25 gram of emulsifier (5% on the oil) in 95 grams of water.

No.	Ratio	10% Emulsion		5% Emulsion	
		Fresh	24 Hrs.	Fresh	24 Hrs.
1	0.05:1	Thick	Thick	Fair	Slightly Gelatinous.
2	0.08:1	do	do	do	6-7 cc. creamed; no free oil.
3	0.10:1	Excellent	Excellent, Thin	Good, Thin	Do.
4	0.12:1	do	do	do	Do.
5	0.15:1	do	Very Good	do	Do.
6	0.2 :1	Very Good	do	do	Do.
7	0.3 :1	Thin, Frothy	Slightly Creaming.	do	Do.
8	0.5 :1	do	do		

These results show that, while self-emulsification is obtained throughout the range of 0.05–0.5 mols of epichlorhydrin per mol of amine, the optimum ratio is about 0.1 to 0.2 mol. Similar tests using 2.5% of the emulsifiers and 5% of the oil solution in the emulsions showed similar results. Larger quantities of the emulsifier up to, for example, 20–30% on the weight of the oil can of course be used if desired, but for most purposes this is not necessary.

What I claim is:

1. A self-emulsifying mineral oil composition comprising mineral oil having dissolved therein a minor quantity not less than 2.5% by weight of the reaction product obtained by heating 0.05 to 0.5 mols of epichlorhydrin with the condensation product of 1 mol of a primary alkylamine of 12–18 carbon atoms with 2 to 10 mols of combined ethylene oxide.

2. A self-emulsifying mineral oil composition comprising mineral oil having dissolved therein emulsifying quantities, not less than 2.5% by weight, of the condensation product of 0.05 to 0.5 mols of epichlorhydrin with one mol of an ethoxyethyloloctadecylamine containing from 2 to 10 mols of combined ethylene oxide for each mol of octadecylamine.

3. A composition according to claim 2 in which the ethoxyethyloloctadecylamine contains from 2 to 6 mols of combined ethylene oxide for each mol of octadecylamine.

4. A self-emulsifying mineral oil composition comprising mineral oil having dissolved therein emulsifying quantities, not less than 2.5% by weight, of the condensation product of from 0.1 to 0.2 mols of epichlorhydrin with 1 mol of an ethoxyethyloloctadecylamine containing from 2 to 10 mols of combined ethylene oxide for each mol of octadecylamine.

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