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RECOVERY OF GUANIDINE PETROLEUM SULFONATES AS OIL DETERGENTS

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This invention relates to improved mineral oil detergents. In one aspect this invention relates to the manufacture of guanidine petroleum sulfonates, particularly suitable as mineral oil detergents. In another aspect this invention relates to the removal of incompletely oil-soluble guanidine sulfonates from a mineral oil containing same together with oil-soluble guanidine petroleum sulfonates by solvent extraction employing a selected class of normally liquid ketones as selective solvents. In another aspect this invention relates to the separation of mineral oil-soluble guanidine petroleum sulfonates from incompletely or difficultly mineral oil-soluble guanidine petroleum sulfonates in mixture therewith. In still another aspect this invention relates to the utilization of a selected class of normally liquid ketones as selective solvents in the recovery of guanidine petroleum sulfonates having a special utility as mineral oil detergents, from a mixture containing same together with other guanidine petroleum sulfonates.

In the co-pending application of William N. Axe and William B. Whitney, Serial Number 217,669, filed March 26, 1951, now Patent No. 2,660,562, in which I am a co-inventor, is disclosed a method for the preparation of guanidine petroleum sulfonates having a special utility as gelation agents and as mineral oil detergents. In another co-pending application of William N. Axe and William B. Whitney, of which I am a co-inventor, Serial Number 238,190, filed July 23, 1951, a continuation-in-part of the first said copending application Serial Number 217,669, are disclosed and claimed guanidine petroleum sulfonates as new compositions. As set forth in the first said co-pending application, a selected petroleum oil fraction can be sulfonated followed by neutralization of the resulting petroleum sulfonic acid with guanidine or a guanidine base, whereby guanidine petroleum sulfonates of varying degrees of oil solubility are formed. The oil-soluble sulfonates thus formed have been found to be excellent oil detergents and the sulfonates of lesser oil solubility have been found to be excellent gelation agents, particularly with reference to the manufacture of greases. As set forth in the first said co-pending application, the guanidine petroleum sulfonates derived from oil fractions containing from 40–70 carbon atoms in the molecule are oil-soluble and are excellent oil detergents and those guanidine petroleum sulfonates derived from oil fractions containing from 20–40 carbon atoms per molecule and polyguanidine polysulfonates derived from oil fractions containing from 70–80 carbon atoms per molecule are less oil soluble and are excellent gelation agents.

In accordance with one method for the manufacture of guanidine petroleum sulfonates of the kind described herein, the following steps are involved; (1) sulfonation; (2) neutralization of the sulfonic acid formed, with guanidine; and (3) separation of oil-soluble sulfonates from oil-insoluble sulfonates.

In the preparation of oil-soluble guanidine petroleum sulfonates (detergents) as primary product, by the sulfonation of a petroleum stock followed by neutralization

of guanidine as discussed above, difficulty has been experienced in separating the less desirable or detrimental incompletely oil-soluble guanidine petroleum sulfonates from the desirable completely oil-soluble guanidine petroleum sulfonates.

In a mineral oil containing both the oil-soluble guanidine petroleum sulfonates and the incompletely oil-soluble guanidine petroleum sulfonates, such as the reaction product resulting from the sulfonation and neutralization described above, the incomplete miscibility of the incompletely oil-soluble sulfonates with the oil is manifest in anomalous viscosities of the oil solution. For example, if the oil solution is heated sufficiently and the viscosities at 100 and 210° F. are measured immediately following such heating (to a temperature of about 130° F.) viscosities and viscosity indices similar to the base oil are obtained. However, if the oil solution is allowed to remain at room temperature for a period of time, say from 6–8 hours, by measurement of viscosity it is found that the vicosity at 210° F. is essentially normal but that the viscosity at 100° F. has increased markedly thus decreasing the viscosity index to a low value. These anomalous viscosities appear to result from the partial solubility of the incompletely oil-soluble sulfonates at the elevated temperature, not yet having separated from the solution at the lower temperature, but having separated and settled therefrom prior to the measurement made several hours later.

Attempts heretofore to extract detergent product, i. e., the oil-soluble guanidine petroleum sulfonates, from the mineral oil containing them together with other guanidine petroleum sulfonates, employing as selective solvent such solvents as benzene, stoddard solvent, pentane, and alcohols, i. e., methyl, ethyl, propyl and butyl, have been unsuccessful, such use of these materials resulting in the formation of slimy or gummy sludge so that the whole solvent-containing mixture cannot be readily filtered, if at all.

In accordance with a basic concept of this invention, a mixture of guanidine petroleum sulfonates of varying degrees of oil solubility and containing completely oil-soluble sulfonates and also sulfonates only difficultly oil-soluble, is dissolved in a normally liquid ketone solvent at an elevated temperature, followed by cooling the resulting solution, under which conditions incompletely oil-soluble guanidine petroleum sulfonates are precipitated and then can be readily separated from the mother liquor by any desirable means such as filtration. The mother liquor contains the oil-soluble petroleum sulfonates which are recovered therefrom as a product of the process.

Although the present invention is applicable to any mixture of guanidine petroleum sulfonates, it is particularly well applied to the reaction mixture resulting from the sulfonation of a petroleum oil followed by neutralization of the petroleum sulfonic acids with guanidine or a guanidine basic salt such as guanidine carbonate. Normally liquid ketones included among those employed in accordance with the process of my invention are those having from 3–11 carbon atoms per molecule. Of these, the preferred ketone solvents are the unsymmetrical alkyl ketones having from 1–4 carbon atoms in one of the alkyl groups. Exemplary of normally liquid ketone solvents employed in the practice of the present invention are acetone, methyl ethyl ketone, methyl-n-propyl ketone, methylisopropyl ketone, methyl-n-butyl ketone, methylisobutyl ketone, and diethyl ketone.

In the practice of this invention a sufficient quantity of the liquid ketone is added to the mixture of guanidine petroleum sulfonates to be treated, to effect complete solution when heated to an elevated temperature described hereafter. Generally an amount of from 1–7 volumes of ketone solvent per volume of the guanidine petroleum sul-

fonate mixture is sufficient for this purpose. Usually 2–4 volumes of ketone solvent per volume of the guanidine petroleum sulfonate mixture is sufficient.

The temperatures employed during the extraction step of this invention are dependent somewhat upon the particular ketone solvent selected, it often being advantageous to heat the total mixture to a temperature near the boiling point of the ketone solvent employed. Thus in the case of methylisobutyl ketone, which has a boiling point of 119° C. the extraction mixture is heated to a temperature of about 100° C. The time required to heat this mixture to the desired temperature is usually sufficient to effect solution of the mixture being treated in the ketone solvent. The extraction mixture thus heated can be cooled to any temperature desired below, say about 50° C., which is advantageously about room temperature or slightly above, for example 20° C.

In carrying out the sulfonation and neutralization process in the manufacture of guanidine petroleum sulfonates from the petroleum stock discussed above, a preferred sulfonation base stock is selected from the more viscous or bright stock fractions of petroleum. More specifically such a sulfonation base stock can consist of a deasphalted and solvent refined petroleum fraction having a viscosity range between about 80 and 700 SUS at 210° F. Another preferred sulfonation stock is propane fractionated-solvent extracted and dewaxed Mid-Continent oil of about 200–230 SUS as 210° F., having a viscosity index of about 85–95 or higher. Similar bright stocks of Pennsylvania or naphthenic origin, while less desirable for such sulfonation, may be used.

As disclosed in the above-said co-pending application, total reaction product, i. e., the mineral oil containing the guanidine petroleum sulfonates can be admixed with an equal volume of an alcohol such as one containing from 2–6 carbon atoms, preferably isopropyl alcohol, and agitated therewith at a temperature near the boiling point of the alcohol at atmospheric pressure, under which conditions the guanidine petroleum sulfonate reaction products and the oil dissolve in the alcohol. Upon cooling the resulting alcohol mixture to about room temperature, i. e., about 20–40° C., a large portion of the solute precipitates from the solution as a gummy viscous liquid, the precipitate, i. e., "alcohol-insoluble" oil comprising an oil solution or dispersion of "oil-soluble" guanidine petroleum sulfonates in major proportions. When using the term "oil-soluble," it is meant the solubility of the material in a lube oil base stock or in a mineral oil present as such in the oil-sulfonation-neutralization reaction mixture. Several properties of the alcohol-insoluble product are listed as follows:

Specific Gravity, 60/60° F.	Gravity ° API at 60° F.	Percent Nitrogen
0.8887	27.7	1.08

This invention is advantageously applied to the extraction of oil-soluble guanidine petroleum sulfonates from an alcohol-soluble or alcohol-insoluble fraction of the kind described above.

In one preferred embodiment of this invention a reaction product of sulfonation of a deasphalted and solvent-refined petroleum fraction, the sulfonic acid in which has been neutralized with guanidine or a guanidine basic salt, is admixed with from 2–4 volumes of an unsymmetrical alkyl ketone containing from 1–4 carbon atoms in one of the alkyl groups, such as methylisopropyl ketone, and heated to a temperature near its boiling point, about 100° C., when employing methylisopropyl ketone, and then cooled to about room temperature. The incompletely oil soluble guanidine petroleum sulfonates are precipitated upon cooling and are readily separated from the cooled mixture by filtration. Oil-soluble guanidine petroleum sulfonates separated from the incompletely oil-soluble sulfonates are present in the mother liquor and are separated therefrom by any desired means, as for example by distillation.

Although I have stated that I prefer to operate the extraction process of this invention at a temperature approaching the boiling point of the ketone solvent, my invention is generally practiced with reference to any suitable extraction temperature such as a temperature within the range of from 60 to 120° C., as measured at about atmospheric pressure.

The extraction pressure employed can be at any suitable level such as within the limits of 10 to 50 p. s. i.

In cooling the extraction mixture subsequent to heating, I have found that temperatures below about 10° C. are generally not required for effecting the desired precipitation of the incompletely oil-soluble guanidine petroleum sulfonates.

This invention is illustrated with reference to the following examples.

Several base oil stocks, defined herein below, were each sulfonated and then neutralized with guanidine, and each resulting oil solution of guanidine sulfonates, containing both oil-soluble and incompletely oil-soluble guanidine sulfonates, was then alcohol extracted, employing isopropyl alcohol as the selective solvent.

Several alcohol insoluble portions obtained as extraction product were subjected to viscosity determination at 100° F. immediately after heating to about 210° F. and also after standing for several hours. The following tabulation demonstrates the anomalous viscosities observed, due to the presence of both oil-soluble and incompletely oil-soluble guanidine petroleum sulfonates:

ALCOHOL-INSOLUBLE FRACTION [3]

Run No.	Base oil	Wt. percent of total Guanidine Petroleum Sulfonates in Base oil	Viscosity, SUS, 100° F.	
			Immediately after heating and cooling	After Standing
1	SAE 10 [1]	20	230	267.7
	SAE 10	0		120.7
2	SAE 30 [2]	20	752	814

[1] A Mid-Continent solvent refined oil.
[2] A Mid-Continent solvent refined oil.
[3] Insoluble in isopropyl alcohol.

An alcohol-insoluble fraction and an alcohol-soluble fraction obtained as products of the type of alcohol extraction described above were further extracted with methyl-isobutyl ketone and the resulting ketone soluble portion (at 25° C.) was subjected to viscosity tests at 100° F. immediately after heating to about 210° F. and also after standing for several hours. The following tabulation demonstrates, by the reproducible viscosities obtained (no anomalous viscosities), the substantial absence of incompletely oil-soluble guanidine petroleum sulfonates and thus the efficiency of methylisobutyl ketone as a selective solvent in the process of this invention.

ALCOHOL-INSOLUBLE FRACTION [2] (PORTION SOLUBLE AT 75° F. IN METHYLISOBUTYL KETONE)

Run No.	Base Oil	Wt. percent of Total Guanidine Petroleum Sulfonates in Base Oil	Viscosity, SUS, Immediately after heating and cooling	100° F. After Standing
1	SAE 10 [1]	5	207.5	207.5

ALCOHOL-SOLUBLE FRACTION [3] (PORTION SOLUBLE AT 75° F. IN METHYLISOBUTYL KETONE)

2	SAE 10 [1]	5	133.0	133.0

[1] Mid-Continent solvent refined oil.
[2] Insoluble in isopropyl alcohol.
[3] Soluble in isopropyl alcohol.

Variation and modification are possible within the scope of the foregoing disclosure and the claims to this invention, the essence of which is the separation of guanidine petroleum sulfonates, especially suitable as mineral oil detergents, from a mixture containing same together with other guanidine petroleum sulfonates, by solvent extraction employing a normally liquid ketone as a selective solvent in accordance with the steps (1) heating the total solvent admixture to a temperature to dissolve all components in the ketone solvent, (2) cooling the reaction mixture thus heated until the undesirable guanidine petroleum sulfonates precipitate from the solvent mixture and (3) recovering the solute from the mother liquor as a guanidine petroleum sulfonate having a special utility as a mineral oil detergent, as a product of the process.

I claim:

1. A process for the separation of mineral oil-soluble guanidine petroleum sulfonates from incompletely mineral oil-soluble guanidine petroleum sulfonates in mixture therewith, comprising admixing with said guanidine petroleum sulfonate mixture at least an equal volume of a normally liquid ketone, heating the resulting admixture to an elevated temperature so as to dissolve all of said guanidine petroleum sulfonates in said ketone and then cooling the said admixture until incompletely oil-soluble guanidine petroleum sulfonates precipitate therefrom, and recovering oil-soluble guanidine petroleum sulfonates from the resulting mother liquor as a product of the process.

2. The process of claim 1, wherein said normally liquid ketone is methylisobutyl ketone.

3. A process for the removal of incompletely oil-soluble guanidine petroleum sulfonates from a petroleum oil containing them together with oil-soluble guanidine petroleum sulfonates, comprising admixing with one volume of said petroleum oil containing said sulfonates from 1 to 7 volumes of a normally liquid dialkyl ketone containing from 3–11 carbon atoms in the molecule and heating the resulting admixture to a temperature above about 50° C., whereby said guanidine sulfonates completely dissolve in said ketone, then cooling said admixture to a temperature below about 50° C., whereby incompletely oil-soluble guanidine petroleum sulfonates precipitate from said ketone mixture, separating said precipitate from said cooled admixture and recovering ketone-soluble product from the resulting mother liquor as a product of the process.

4. The process of claim 3 wherein said ketone is an unsymmetrical ketone containing from 1–3 carbon atoms in one of the alkyl groups.

5. The process of claim 3, wherein all of said petroleum oil mixture of guanidine petroleum sulfonates is insoluble in isopropyl alcohol at temperatures below about 40° C.

6. The process of claim 3, wherein all of said petroleum oil mixture of guanidine petroleum sulfonates is soluble in isopropyl alcohol at temperatures below about 40° C.

7. In the sulfonation of a petroleum oil followed by neutralization of resulting petroleum sulfonic acids with guanidine to produce oil-soluble guanidine petroleum sulfonates as lube oil detergents, wherein incompletely oil-soluble guanidine petroleum sulfonates are also formed and are present as contaminants in the resulting neutralization reaction mixture, the improvement providing for the removal of said incompletely oil-soluble sulfonates from the said reaction mixture, comprising admixing with one volume of said reaction mixture with from 2 to 4 volumes of an unsymmetrical dialkyl ketone containing from 3–11 carbon atoms in the molecule and from 1–3 carbon atoms in one of the alkyl groups and heating the resulting admixture to a temperature above about 50° C. and not higher than the boiling point of said ketone, thereafter cooling said admixture to a temperature below 50° C., whereby during said heating all guanidine petroleum sulfonates dissolve in said admixture and then precipitate therefrom upon said cooling, and recovering ketone-soluble sulfonates from the resulting mother liquor as a product of the process.

8. The improvement of claim 7 wherein said reaction mixture is formed by sulfonation and neutralization of a deasphalted petroleum fraction having a viscosity within the range of 80–700 SUS @ 210° F.

9. The improvement of claim 7, wherein said normally liquid ketone is methylisobutyl ketone.

10. In the separation of oil-soluble guanidine petroleum sulfonates from incompletely oil-soluble guanidine petroleum sulfonates in mixture therewith, the improvement comprising contacting such a mixture at an elevated temperature with a normally liquid ketone to dissolve said oil-soluble sulfonates and said incompletely oil-soluble sulfonates in the said ketone solvent and then cooling the resulting solvent mixture to precipitate said incompletely oil-soluble sulfonates as a ketone insoluble fraction.

11. A process for the separation of mineral oil-soluble guanidine petroleum sulfonates from incompletely mineral oil-soluble guanidine petroleum sulfonates in mixture therewith, comprising admixing with said guanidine petroleum sulfonate mixture a normally liquid ketone, heating the resulting admixture to an elevated temperature so as to dissolve at least a portion of the said guanidine petroleum sulfonates in said ketone and then cooling the resulting solution until incompletely oil-soluble guanidine petroleum sulfonates precipitate therefrom, whereby oil-soluble guanidine petroleum sulfonates thus separated from incompletely oil-soluble guanidine petroleum sulfonates are retained in the resulting mother liquor, and recovering at least one of the said guanidine petroleum sulfonates thus separated as product of the process.

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