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REFINING MINERAL OILS

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This invention relates to improvements in the refining of hydrocarbon oils and in particular to improvements in the refining of white oils such as medicinal mineral oils, technical white oils, and the like, to obtain increased yields of oil and preferential oil-soluble water non-emulsifiable sulfonic compounds.

In the preparation of highly refined petroleum oils of the type of insulating oils, turbine oils, technical white oils, and mineral medicinal oils, the oils are treated successively with a number of portions of concentrated or fuming sulfuric acid. A variety of sulfur-containing compounds are formed by the chemical reactions of the treating operation, including sulfonic acids, organic esters of sulfuric acid, partial esters of sulfuric acid, etc. Most of these compounds are relatively insoluble in the oils under the treating conditions and separate from the oil, together with unreacted acid, as a sludge which is separated from the oil after each acid treatment. Some of the sulfonic acids are preferentially oil soluble; these remain in the oil and can be removed therefrom by neutralizing the acid-treated oil with caustic soda, caustic potash or ammonia, to form sulfonic acid soaps or sulfonates, and extracting these sulfonates from the oil by treatment with 50% to 80% aqueous alcoholic solutions or other suitable means. Because of the characteristic mahogany color of these sulfonates they are known in the petroleum art as mahogany soaps.

While the preferential oil-soluble sulfonates or sulfonic acids, hereinafter generically called sulfonic compounds, from different stocks, and by different acid treatments, as a class are all soluble in oil, they all do not behave similarly in water solubility and/or emulsibility. That is, certain of the preferential oil-soluble sulfonic compounds form relatively stable emulsions with water, while other types of the preferential oil-soluble sulfonic compounds do not form emulsions with water or are difficultly emulsifiable with water.

Thus preferential oil-soluble sulfonic compounds obtained by treating a petroleum oil having a Saybolt Universal viscosity at 100° F. of less than about 150 seconds, with about 3 to about 4 pounds of fuming sulfuric acid per gallon of oil are characterized by their ability to readily emulsify with water to give stable emulsions. These sulfonic compounds therefore, are well suited for the preparation of soluble oil compositions.

Treating an oil of the same type as the above, or an oil having a Saybolt Universal viscosity at 100° F. above about 225 seconds with about 7 to about 8 pounds of fuming sulfuric acid per gallon of oil, will produce preferential oil-soluble sulfonic compounds which are substantially non-emulsifiable with water. That is, stable emulsions with water cannot be formed, and hence they are unsuited for use in the preparation of soluble oil

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compositions. However, such sulfonic compounds are of value for other purposes, such as, for example, as rusting and/or corrosion inhibitors in slushing or anti-rust compositions. Hereinafter and in the appended claims, sulfonic compounds of this type, which are preferentially oil-soluble but substantially non-emulsifiable with water, will be referred to as "preferential oil-soluble, water non-emulsifiable sulfonic compounds," "preferential oil-soluble, water non-emulsifiable sulfonic acids," or "preferential oil-soluble, water non-emulsifiable sulfonates."

By the term "water non-emulsifiable" as used herein and in the appended claims, is meant an oil-soluble sulfonic compound which does not pass the emulsion test, described by F. M. Archibald in the article "Analysis of petroleum oil-soluble sulfonic acid soaps," on page 611 of September 15, 1941, issue of the Analytical edition of Industrial and Engineering Chemistry.

In the manufacture of white oils, the process commonly employed is the treatment of a petroleum oil, and especially a petroleum distillate, with large quantities of sulphuric acid. In general, fuming sulphuric acid of about 104½% of H_2SO_4 equivalent is employed and the acid is customarily applied to the oil in small portions or "dumps" of about one-half pound to about one pound of acid per gallon of oil. Thus, in preparing a medicinal white oil, approximately 8 pounds of fuming sulphuric acid is used per gallon of oil, applied in 8 or more successive dumps, the acid sludge being settled and withdrawn after each dump. Treating the oil in this manner results in a relatively low yield of finished oil and low yield of preferential oil-soluble, water non-emulsifiable sulphonic acids or sulphonic acid soaps.

It is an object of the invention to provide a method of treating petroleum oils with sulphuric acid which will result in a maximum yield of preferential oil-soluble water non-emulsifiable sulphonic acids or sulphonic acid soaps. Another object of the invention is to provide a method for manufacturing white oils with fuming sulphuric acid which will give a maximum yield of refined oil and preferentially oil-soluble water non-emulsifiable sulphonic acids of the soaps thereof with a minimum acid requirement. It is another object of the present invention to provide a method of refining white mineral oils by treatment with sulphuric acid which will result in a maximum yield of treated oil.

In accordance with the present invention, the foregoing objects are attained by treating a hydrocarbon oil, such as petroleum oil, having a Saybolt Universal viscosity at 100° F. above about 225 seconds, for example, from about 250 seconds to about 1000 seconds, and preferably from about 400 to about 800 seconds, with from about 2

pounds to about 4 pounds of concentrated sulphuric acid, preferably fuming sulphuric acid, per gallon of oil, separating the resultant acid sludge, extracting the preferential oil-soluble water non-emulsifiable sulfonic acid or soap from the treated oil with alcohol, removing the last traces of alcohol from the extracted oil and retreating the oil with about 1 pound to about 3 pounds of concentrated sulphuric acid, and preferably fuming sulphuric acid, per gallon of oil, and again extracting the preferential oil-soluble water non-emulsifiable sulfonic acids with alcohol from the sour oil. The alcohol extracted sour oil is then neutralized, steamed and blown bright, or alternatively extracted sour oil can be neutralized, the neutralized oil again extracted with alcohol and the oil finally blown bright and, if desired treated with clay, such as by clay percolation through a decolorizing clay such as Attapulgus clay. In applying the sulphuric acid to the oil in either the first or the second stages, the oil is preferably added in dumps of one-half pound of acid per gallon of oil.

After the first acid treatment stage in which 2 to 4 pounds of acid per gallon of oil is employed, the preferential oil-soluble, water non-emulsifiable sulfonic acids may be extracted as such with alcohol, preferably ethyl alcohol, or they may be converted into the soap by treatment with a neutralizing agent, such as caustic soda, caustic potash or the like, and the sulfonic soaps so formed extracted from the oil with alcohol; however, after the second acid treatment stage the sulfonic acids must be extracted as such.

In the acid treating stages temperatures of from about 40° F. to about 250° F., and preferably from about 60° F. to about 100° F. are maintained. The contact time of the acid with the oil is preferably within the range of about 150 to 250 minutes for a treating temperature range of 60° to 100° F. However, a contact time as low as three to thirty minutes may be used with treating temperatures within the range of 100° to 250° F.

The extraction of the preferential oil-soluble, water non-emulsifiable sulfonic acids or the soaps thereof from the acid treated oil is accomplished preferably with alcohol of about 60% concentration and usually in the range of about 55% to about 70%, the amount of alcohol required for the extraction being within the range of from about 10 gallons to about 30 gallons of alcohol per 100 gallons of oil.

The alcoholic solutions of preferential oil-soluble, water non-emulsifiable sulfonic acids or the soaps thereof from each of the alcohol extraction stages can be treated, such as by distillation, to remove the alcohol and the preferential oil-soluble, water non-emusifiable sulfonic compounds recovered. If the preferential oil-soluble, water non-emulsifiable sulfonic compounds are extracted as the acid in the first extraction stage, the alcoholic extract from the first extraction stage may be combined with the alcoholic solution of preferential oil-soluble water non-emulsifiable sulfonic acids from the second extraction stage and the alcohol removed from the combined fractions. The acids can then be converted to the soap by neutralization with an alkaline reagent such as caustic soda, caustic potash, or the like. If the preferential oil-soluble water non-emulsifiable sulfonic compounds are extracted as the soap, the preferential oil-soluble water non-emulsifiable sulfonic acids extracted from the second extraction stage can be converted to the soap by neutralization and the alcoholic solutions of the soaps combined. The soaps can then be recovered by means such as distillation.

It has been found that in the first acid treatment stage, a portion of the spent acid sludge from the second acid treatment stage can be recycled and used to replace a portion of a fuming sulphuric acid normally used in the first acid treating stage.

The effectiveness of the present invention is demonstrated by the data of the following examples which are given by way of illustration and are not intended to be limitative of the scope thereof.

Example.—A petroleum distillate having a Saybolt Universal viscosity at 100° F. of about 233 seconds was treated with 3 pounds of fuming sulphuric acid per gallon of distillate in ½ pound dumps. After removal of the acid sludge after the last acid dump and neutralization of the oil, it was extracted (sour) with alcohol and the last traces of the alcohol removed from the oil by distillation. The oil was then treated with an additional 2½ pounds of fuming acid per gallon of distillate in ½ pound dumps and the sour oil was extracted with alcohol after removal of the acid sludge. The extracted oil was then neutralized, steamed and blown bright. The yield of finished oil and of preferential oil-soluble, water non-emulsifiable sulfonic acids recovered are given in the following Table I in comparison with the yield of oil and of mahogany acids obtained by treating the oil in the usual manner with 7 pounds of fuming sulphuric acid per gallon of distillate without an intermediate extraction step.

Table I

Method	Total lbs. acid/gal. of distillate	Yield of finished oil, vol. percent	Yield of 100% preferential oil-soluble, water non-emulsifiable sulfonic acid, vol. percent on distillate
Old	7.0	50.3	1.32
New	5.5	53.3	6.07

The above data show the increased yield of oil and sulfonic acid obtained with a lower acid requirement when the oil is treated in accordance with the present invention.

The data represented in Table II below illustrate the improvements obtained by treating coastal oils of 600 seconds Saybolt viscosity in accordance with the present invention over that obtained by treating in the conventional manner. In each of the first three tests the oil was treated with fuming sulphuric acid in two stages with an intermediate alcohol extraction after the first acid treatment stage. In test No. 1 the oil was treated first with 3 pounds of fuming sulphuric acid in ½ pound acid dumps, the oil neutralized with caustic soda and the neutralized oil then extracted with 60% alcohol to remove the preferential oil-soluble, water insoluble sulfonates. The oil was then given an additional treatment with 3½ pounds of fuming sulphuric acid per gallon of oil in ½ pound dumps and the sour oil extracted with 60% alcohol. In test No. 2 the distillate oil was treated first with 3½ pounds fuming sulphuric acid per gallon of distillate in ½ pound dumps and the sour oil neutralized with caustic soda. The preferential oil-soluble, water non-emulsifiable sulfonates were then extracted with 60% alcohol, and the oil then treated with 2½ pounds of fuming sulphuric acid per gallon

of distillate in ½ pound dumps. The preferential oil-soluble, water non-emulsifiable sulfonic acids were then extracted from the sour oil with 60% alcohol. In test No. 3, the oil was first treated with 4 pounds of fuming sulphuric acid per gallon of distillate in ½ pound dumps and preferential oil-soluble, water non-emulsifiable sulfonic acids extracted from the sour oil with 60% alcohol. The oil was then given an additional treatment with 2 pounds of fuming sulphuric acid per gallon of distillate in ½ pound dumps and the preferential oil-soluble, water non-emulsifiable sulfonic acids extracted from the sour oil with 60% alcohol. The yields of finished oil and of the preferential oil-soluble water non-emulsifiable sulfonic acids are given in the table. For comparison, data based on conventional procedure are given, in which the oils were treated in the conventional manner with 8 pounds of fuming extract acid per gallon of distillate oil without an intermediate alcohol extraction step.

Table II

Test No.	Lbs. acid/gal. distillate		Alcohol extraction 60— alcohol		Yields		
					Finished oil, vol. per cent	Alcohol extract	
	1st stage	2nd stage	1st stage	2nd stage		100% sulfonic acids,[1] vol. per cent	Oil, vol. per cent
1	3	3.5	Alkaline	Sour	53.3	4.88	4.67
2	3.5	2.5	do	do	50.7	3.89	7.63
3	4.0	2.0	Sour	do	54.6	2.63	2.38
Conventional procedure—8 lbs. acid per gallon distillate, extracted sour after total acid treat with no intermediate alcohol extraction.					51.2	.75	1.20

[1] Preferential oil-soluble, water non-emulsifiable acids.

The increased yield of preferential oil-soluble water insoluble sulfonic acids obtained by treating oils of Saybolt Universal viscosity at 100° F. above 225 seconds by the method of the present invention is further demonstrated by data in Table III below. These data were obtained by treating an oil having a Saybolt Universal viscosity at 100° F. of about 600 seconds, and an oil having a Saybolt Universal viscosity at 100° F. of about 125 seconds with sixteen successive one-half pounds of fuming sulfuric acid per gallon of oil, and determining the amount and type of preferential oil-soluble sulfonic acid extracted from the sour oil after each one-half pound acid dump.

Table III

No. of 0.5 lb. of 104.5% H_2SO_4 per gal. of dist.	Total lbs. of 104.5% acid per gal. dist.	High viscosity oil lbs. of 100% sulfonic acid in sour oil from 100 gal. dist.	Low viscosity oil lbs. of 100% sulfonic acid in sour oil from 100 gal. distillate
1	0.5		
2	1.0		12.6
3	1.5		
4	2.0	23.0	30.3
5	2.5		
6	3.0	[1] 34.3	[2] 35.0
7	3.5		
8	4.0	[1] 31.0	[2] 35.8
9	4.5		
10	5.0	[1] 23.8	[2] 21.0
11	5.5		
12	6.0	[1] 17.0	
13	6.5		
14	7.0	[1] 10.8	
15	7.5		
16	8.0	[1] [c] 6.3	[1] [c] 10.0

[1] Preferential oil-soluble, water insoluble sulfonic acids.
[2] Preferential oil-soluble, water soluble sulfonic acids.
(c) Conventional methods for obtaining preferential oil-soluble, water insoluble sulfonic compounds.

The above data show the large yield increase of preferential oil-soluble, water insoluble sulfonic compounds obtained by the present invention over that obtained by treating oils by the conventional method with eight pounds of concentrated sulfuric acid per gallon of oil to obtain the same type of sulfonic compound.

As shown by the data of the above Tables I and II, increased yields of finished oil and increased yields of preferential oil-soluble, water non-emulsifiable sulfonic acids and sulfonates are obtained by treating petroleum distillates in accordance with the present invention. The present invention not only provides an improved method for obtaining increased yields of finished oil and preferential oil-soluble, water non-emulsifiable sulfonic acids or soaps, but also results in a 25% or greater reduction in acid requirements to obtain the same white oil quality as well as the increased yields.

While the method of treating and purifying mineral oils herein described is well suited for accomplishing the purposes of the present invention, it is not intended to limit the invention to the specific embodiments described herein, as various modifications may be made without departing from the spirit of the invention.

I claim:

1. The method of obtaining increased yields of preferential oil-soluble, water non-emulsifiable sulfonic compounds from petroleum oils comprising treating a viscous hydrocarbon oil having a Saybolt Universal viscosity at 100° F. above about 225 seconds with from about 2 pounds to about 4 pounds of concentrated sulfuric acid per gallon of oil, separating the acid sludge from said treated oil, extracting perferential oil-soluble water non-emulsifiable sulfonic compounds from the acid treated oil with alcohol, removing alcohol from the extracted oil, treating the alcohol extracted oil with from about 1 pound to about 3 pounds of concentrated sulfuric acid per gallon of oil, separating the acid sludge formed, extracting preferential oil-soluble water non-emulsifiable sulfonic acid from the acid treated oil with alcohol, and removing the alcohol from both alcohol extracts of the preferential oil-soluble water nonemulsifiable sulfonic compounds.

2. The method described in claim 1, in which the concentrated sulfuric acid is fuming sulfuric acid.

3. The method described in claim 1, in which the concentrated sulfuric acid is applied in ½ pound dumps.

4. The method described in claim 1, in which the preferential oil-soluble sulfonic compounds are extracted with alcohol of from about 55% to about 70% concentration.

5. The method of obtaining increased yields of preferential oil-soluble water non-emulsifiable sulfonic compounds from petroleum oils comprising treating a viscous hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of from about 250 seconds to about 1000 seconds with from about 2 pounds to about 4 pounds of concentrated sulfuric acid per gallon of oil, separating the acid sludge from said oil, neutralizing the acid treated oil, extracting preferential oil-soluble water non-emulsifiable sulfonates from the neutralized oil with alcohol, removing the last traces of alcohol from the extracted oil, treating the alcohol extracted oil with about 1 to about 3 pounds of concentrated sulfuric acid per gallon of oil, separating the acid sludge

formed, extracting preferential oil-soluble water non-emulsifiable sulfonic acids from the acid treated oil with alcohol, and removing the alcohol from both alcohol extracts of the preferential oil-soluble sulfonic compounds.

6. The method described in claim 5, in which the concentrated sulfuric acid is fuming sulfuric acid.

7. The method of obtaining preferential oil-soluble water non-emulsifiable sulfonic compounds from petroleum oils comprising treating a petroleum mineral oil distillate having a Saybolt Universal viscosity at 100° F. above about 225 seconds with about three pounds of fuming sulfuric acid per gallon of oil, separating the acid sludge from the sour oil, neutralizing the sour oil, extracting a preferential oil-soluble water non-emulsifiable sulfonic acid soap from the neutralized oil with alcohol, freeing the oil of entrained alcohol, re-treating the three pound acid-treated oil with about three pounds more of fuming sulfuric acid, separating the acid sludge, extracting the preferential oil-soluble

water non-emulsifiable sulfonic acid from the six pound acid-treated oil with alcohol and neutralizing the extracted preferential oil-soluble water non-emulsifiable sulfonic acids.

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