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EXTRACTION OF SULFURIC ACID SLUDGE

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This invention relates to improvements in the recovery of petroleum sulfonic acids from acid sludge, and more particularly to the recovery of preferentially oil-soluble sulfonic acids and water-soluble sulfonic acids from unhydrolyzed sulfuric acid sludges.

In the refining of petroleum oils with sulfuric acid, such as concentrated or fuming sulfuric acid, mixtures of sulfonic acids are produced. These sulfonic acids vary over a wide range in the degree of water-solubility and of oil-solubility. Some of these sulfonic acids, which are reddish-brown in color and which are generally referred to as mahogany acids, are preferentially oil-soluble. Another class of these sulfonic acids found in the sludge layer, which because of their greenish color are commonly referred to as green acids are preferentially water-soluble. These so-called green acids are in fact mixtures of very water-soluble sulfonic acids which are known in the art as black acids, intermediate water-soluble detergent type sulfonic acids and preferentially oil-soluble sulfonic acids, known in the art as brown acids. The so-called black acids are more water-soluble than the intermediate water-soluble detergent type sulfonic acids, while the so-called brown acids, although preferentially oil-soluble, are less oil-soluble than are the mahogany acids.

In the usual refining process, the petroleum oil is treated with strong sulfuric acid, generally fuming sulfuric acid, and the acid sludge which is formed is separated from the acid treated oil. From the acid treated oil there are recovered the preferentially oil-soluble sulfonic acids or the so-called mahogany acids. In the acid sludge there are found the black acids, the intermediate water-soluble detergent type sulfonic acids, and the so-called preferentially oil soluble brown sulfonic acids. Heretofore, the preferentially water-soluble sulfonic acids were recovered from the acid sludge as so-called green acids, by extraction with water, water-soluble solvents, or with mixtures of certain organic solvents and water. The extract so recovered from the acid sludge contained substantial amounts of black acids which materially decrease the detergency value of the intermediate water-soluble detergent type sulfonic acids. Also, since no attempt was made to selectively extract the sulfonic acids, the preferentially oil-soluble brown acids were lost in the so-called green acids.

It is an object of the present invention to provide a method of recovering preferentially oil-soluble sulfonic acids and intermediate water-soluble detergent type sulfonic acids from unhydrolyzed sulfuric acid sludges, resulting from the treatment of hydrocarbon oils with concentrated or fuming sulfuric acid. Another object of the invention is to provide a method of selectively extracting intermediate water-soluble detergent type sulfonic acids and preferentially oil-soluble sulfonic acids from sulfuric acid sludges resulting from the treatment of viscous petroleum oils with concentrated or fuming sulfuric acid.

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We have discovered that the intermediate preferentially water-soluble detergent type sulfonic acids and the preferentially oil-soluble sulfonic acids found in sulfuric acid sludges can be selectively recovered from said sludges by extracting the same with a chlorinated aliphatic or aromatic hydrocarbon solvent, preferably the former. Examples of suitable chlorinated hydrocarbons for this purpose are carbon tetrachloride, chloroform, amyl chloride, amylene chloride, dichloroethylene, dichloromethane, dichloropentanes, ethyl chloride, methyl chloride, propylene dichloride, chloronaphthalenes, chlorinated alkylnaphthalenes, chlorobenzene, chlorinated alkylbenzenes and the like. While each of the named chlorinated hydrocarbons is effective for the herein-described purpose, it is not to be implied that all of them are equally effective. While we prefer to use chlorinated aliphatic hydrocarbons, some of the named chlorinated aliphatic hydrocarbons will be found to be more effective than others; we have found carbon tetrachloride and chloroform to be very well suited for this purpose. The ratio of chlorinated hydrocarbon solvent to the volume of unhydrolyzed sludge to be extracted can vary from about 0.5:1 to 5:1; although, we prefer to use ratios of from 1:1 to 3.5:1. Temperatures employed in extracting the intermediate water-soluble detergent type sulfonic acids and the preferentially oil-soluble sulfonic acids from the unhydrolyzed acid sludge can vary from about 50° F. to about 150° F., and preferably from about 75° F. to about 100° F. For the most efficient extraction, it is highly desirable to provide means for intermittently contacting the unhydrolyzed acid sludge with the solvent. Suitable contact can be obtained by means of high speed propeller type stirrers or by orifice mixers; either type giving the desired degree of stirring and maximum action.

In accordance with the present invention, an unhydrolyzed sulfuric acid sludge resulting from the treatment with fuming sulfuric acid or concentrated sulfuric acid of a viscous hydrocarbon oil, that is, a hydrocarbon oil having a Saybolt

Universal viscosity at 100° F. above about 45 seconds, is thoroughly mixed in the proper predetermined ratio with the chlorinated hydrocarbon solvent. After suitable contacting, the mixture of sludge and solvent is settled to permit stratification of the sludge and solvent layers and the chlorinated hydrocarbon solvent layer separated from the acid sludge layer. The former contains the intermediate water-soluble detergent type sulfonic acids and any preferentially oil-soluble sulfonic acids which may have been present in the unhydrolyzed sulfuric acid sludge, while the latter contains the preferentially water-soluble black acids and unreacted sulfuric acid. The sulfonic acids extracted from the acid sludge with the chlorinated hydrocarbon solvent can be converted to the sulfonate by neutralization and freed of the solvent to obtain a mixture of sulfonates.

While water-soluble detergent type sulfonic acids of the herein described type are recoverable by the present invention from petroleum oils having Saybolt Universal viscosities at 100° F. above about 45 seconds Saybolt, the better yields are obtained from oils having Saybolt viscosities at 100° F. between about 70 seconds and about 350 seconds.

and suitable as wetting and detergent agents. As another alternative, the unhydrolyzed sulfuric acid sludge can be extracted with a mixture of chlorinated hydrocarbon solvent and a hydrocarbon solvent of the herein described type to extract sulfonic acids of varying water-solubility depending upon the relative quantities of the two components used. For example, a mixture containing a greater ratio of the chlorinated aliphatic hydrocarbon will extract sulfonic acids which will form sulfonates giving more pronounced wetting and detergent properties.

The recovery of intermediate water-soluble sulfonic acids by extraction with a chlorinated aliphatic hydrocarbon is illustrated by the data tabulated in the following table. These data were obtained by treating a hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of 75–80 seconds with two pounds of fuming acid, drawing off the acid sludge, then treating with one-half pound of fuming acid and drawing off the acid sludge which then was extracted with carbon tetrachloride and with chloroform. For comparison, data are presented on the extraction of the same unhydrolyzed acid sludge with a petroleum naphtha and with a blend of petroleum naphtha and carbon tetrachloride.

Table

Solvent	Volume Ratio of Solvent to Sludge	Percent Yield Extracted Sulfonic Acid Based on Sludge		
		Total Sulfonate	Oil-Soluble Sulfonate	Intermediate Water-Soluble Detergent Type Sulfonate
Naphtha	2:1	12.6	12.6	0
80% Naphtha, 20% Carbon tetrachloride	2:1	18.8		
Carbon tetrachloride	2:1	47	27	20
Chloroform	2:1	81	32	49

When desired the intermediate water-soluble detergent type sulfonic acids can be selectively separated from the preferentially oil-soluble sulfonic acids by neutralizing the chlorinated solvent extract, removing the solvent from the neutralized product, if desired, and subsequently extracting sulfonates with a hydrocarbon oil, preferably a distillate having a maximum ASTM distillation temperature of not more than about 500° F., and preferably having a distillation range of from about 150° F. to about 350° F. and containing not more than about 5% aromatic hydrocarbons. Suitable hydrocarbon solvents are light petroleum oils and petroleum naphthas, particularly virgin naphthas, of the desired distillation characteristics. The hydrocarbon solvents selectively extract the preferentially oil-soluble sulfonates from the intermediate water-soluble sulfonates. As an alternative method, the unhydrolyzed sulfuric acid sludge can first be extracted with a hydrocarbon solvent of the above described type to remove the preferentially oil-soluble sulfonic acids and the acid sludge then extracted with a chlorinated hydrocarbon solvent, preferably a chlorinated aliphatic hydrocarbon solvent, to remove the intermediate water-soluble detergent type sulfonic acid from the acid sludge. Each of the extracts can then be neutralized and freed of the respective solvents to produce sulfonates which are preferentially oil-soluble in one case, and in the other sulfonates which are soluble in water

The above data demonstrate that extracting the acid sludge with a petroleum naphtha yielded only 12.6% of an oil-soluble sulfonic acid, while a blend of 80% of the petroleum naphtha and 20% of carbon tetrachloride resulted in a sulfonate yield of 18.8%. When the acid sludge was extracted with carbon tetrachloride, a 47% yield of total sulfonates was obtained. When these sulfonates were further extracted with a mineral oil having a Saybolt Universal viscosity of about 180 seconds at 100° F., a fraction representing 27% of oil-soluble sulfonates and a fraction representing 20% of intermediate water-soluble sulfonates were obtained. When the acid sludge was extracted with chloroform, an 81% yield of the total sulfonates was obtained. When the chloroform extract was further extracted with the mineral oil, a fraction representing 32% of oil-soluble sulfonates and a fraction representing 49% of intermediate water-soluble sulfonate were obtained. The above data demonstrate that the herein described invention provides an effective means of recovering from sulfuric acid sludges preferentially oil-soluble sulfonic acids and intermediate water-soluble detergent type sulfonic acids with the exclusion of the undesirable preferentially water-soluble black acids. Alternately, a hydrocarbon solvent can be added to the solution of extracted sulfonic acids in chlorinated hydrocarbon, thereby precipitating water-soluble detergent type sulfonic acids. The water-soluble

detergent type sulfonic acid soaps possess good wetting properties.

In extracting the water-soluble detergent type sulfonic acids with a chlorinated hydrocarbon solvent in accordance with the present invention, it is essential that the extraction be carried out in the absence of any substantial amount, that is, not more than about 1%, of added water, in order to avoid the extraction of undesirable black acids.

The term "intermediate water-soluble detergent type sulfonic acids" as used herein and in the appended claims includes those sulfonic acids recovered from unhydrolyzed sulfuric acid sludges which are water-soluble to the exclusion of any substantial quantities of preferentially water-soluble black acids. The term "intermediate water-soluble sulfonates" means the salt of such sulfonic acids.

The term "strong sulfuric acid" as used herein and in the appended claims includes concentrated sulfuric acid of at least about 95% strength, and fuming sulfuric acids.

While we have described our invention by way of preferred embodiments, other modifications may be made without departing from the scope and spirit of this invention. We, therefore, include within the scope of our invention such modifications as come within the spirit of the appended claims.

We claim:

1. The method of recovering intermediate water-soluble sulfonic acids from unhydrolyzed sulfuric acid sludge containing water-soluble black sulfonic acids, intermediate water-soluble detergent-type sulfonic acids and preferentially oil-soluble sulfonic acids, resulting from the treatment of hydrocarbon oils with strong sulfuric acid, comprising extracting said acid sludge with a chlorinated hydrocarbon solvent, in the absence of added water, separating the chlorinated hydrocarbon extract containing intermediate water-soluble detergent-type sulfonic acids and preferentially oil-soluble sulfonic acids, from the acid sludge, and extracting preferentially oil-soluble sulfonic acids from the chlorinated hydrocarbon extract with a predominantly aliphatic hydrocarbon solvent.

2. The method of claim 1 in which the chlorinated hydrocarbon solvent is a chlorinated aromatic hydrocarbon.

3. The method of claim 1 in which the chlorinated hydrocarbon solvent extract is neutralized prior to being extracted with the predominantly aliphatic hydrocarbon solvent.

4. The method of recovering intermediate water-soluble detergent-type sulfonic acids from unhydrolyzed sulfuric acid sludge containing water-soluble black sulfonic acids, intermediate water-soluble detergent-type sulfonic acids and preferentially oil-soluble sulfonic acids resulting from the treatment of hydrocarbon oils with strong sulfuric acid comprising extracting said unhydrolyzed sulfuric acid sludge with a chlorinated aliphatic hydrocarbon in the absence of added water, separating the chlorinated aliphatic hydrocarbon extract containing the intermediate water-soluble detergent-type sulfonic acids and preferentially oil-soluble sulfonic acids from the acid sludge and extracting preferentially oil-soluble sulfonic acids from the chlorinated aliphatic hydrocarbon extract with a predominantly aliphatic hydrocarbon solvent.

5. The method of claim 4 in which the hydrocarbon solvent is a petroleum naphtha having a maximum boiling point of less than about 500° F.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,087,888	Petroff	Feb. 17, 1914
1,319,027	Divine	Oct. 14, 1919
1,409,590	Salatha	Mar. 14, 1922
1,474,933	Humphreys	Nov. 20, 1923
2,223,194	Thompson	Nov. 26, 1940
2,263,041	Lazar et al.	Nov. 18, 1941
2,320,738	Jenkins	June 1, 1943
2,328,931	Steik	Sept. 7, 1943
2,368,452	Dawson	Jan. 30, 1945

FOREIGN PATENTS

Number	Country	Date
271,433	Germany	Mar. 11, 1914
85,326	Austria	Jan. 15, 1921
773,656	France	Nov. 23, 1934