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BREAKING PETROLEUM EMULSIONS

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This invention relates to the breaking of petroleum emulsions of the water-in-oil type and is specifically concerned with an improvement on the process described in our copending application Serial No. 391,708, filed May 3, 1941, issued April 20, 1943, as Patent No. 2,317,050, according to which such emulsions are broken by means of a water soluble, oil insoluble mahogany sulfonate.

Sulfonation of petroleum oils produces, as is well known, two distinct types of petroleum sulfonic acids, namely, the oil layer or mahogany sulfonic acids, and the sludge or green sulfonic acids. Thus, when the petroleum oil is sulfonated, the mahogany acids, being oil soluble, remain in the oil and are later removed therefrom; whereas, the green acids, being oil insoluble, settle out with the sludge.

As a consequence, there has grown to be a well established distinction between mahogany and green acids on the basis of the preferential oil solubility and water insolubility of the former, and the oil insolubility and water solubility of the latter.

Contrary to this well-established and universal opinion, it is disclosed in U. S. Patent No. 2,266,084, issued December 16, 1941, that by observing certain criteria, there can be produced oil soluble mahogany sulfonic acids which form salts that are oil insoluble and water soluble.

In breaking petroleum emulsions heretofore, it often has been proposed to use the petroleum green acids; or the sludge, containing the green acids; or the water soluble, oil insoluble salts of the green acids. There also have been proposals of using the green sulfonic bodies in conjunction with mahogany sulfonic bodies.

We have disclosed in our said prior application that water soluble, oil insoluble salts or other derivatives of mahogany sulfonic acids are excellent demulsifiers for petroleum emulsions, and in fact, are surprisingly superior to green sulfonic acids or green sulfonates for such purposes.

In general, the mahogany sulfonic acids with which this invention is concerned may be produced by relatively light sulfonation of petroleum oils containing a substantial amount of cyclic hydrocarbons. Thus, by using sulfuric acid of less than oleum strength on the selected petroleum stocks, we are able to obtain the desired mahogany sulfonic acids. In the event that the sulfonic acids are to be obtained from a sulfonation operation which employs multiple acid treat wherein part of the treats are of less than oleum strength, and part of the treats are with oleum, the desired mahogany sulfonic acids can be obtained by effecting their separation from the oil before carrying out the oleum treats.

A preferred petroleum stock for the preparation of our mahogany acids comprises Coastal or naphthenic distillates of the type used as transformer oil stocks. For instance, we have found that a Coastal distillate, having a viscosity between about 50 and about 100 seconds Saybolt Universal viscosity at 100° F., and having a pour-point below 0.0° F. before dewaxing, is highly suited for the production of the type mahogany sulfonic acids with which we are concerned.

The formation of these mahogany sulfonic acids, which are capable of forming oil insoluble, water soluble salts, may be further illustrated by the following specific examples:

Type oil	Saybolt Univ. viscosity at 100° F.	Sulfuric acid used in treat per bbl. oil	Property of sodium sulfonate of sulfonic acids
Coastal distillate.	54 to 59 sec..	43 lbs. of 93% acid (added in a plurality of treats).	Highly water soluble and oil insoluble.
Do.....	54 to 59 sec..	70 lbs. of 98% acid (added in a plurality of treats).	Highly water soluble and oil insoluble.
Do.....	72 to 79 sec..	50 lbs. of 98% acid (added in a plurality of treats).	Highly water soluble and oil insoluble.

The water soluble, oil insoluble mahogany sulfonates and the sulfonic acids from which they are derived, possess such different characteristics from those encountered in the ordinary or conventional mahogany sulfonic acid products, that they are best recovered from the acid treated oil stock by means of an "acid jelly." Thus, after the oil is sulfonated and settled to separate sludge, the remaining sour oil is treated with a small amount of water, for example, 1%, whereby an "acid jelly" is formed in the oil. This "acid jelly," which contains the mahogany sulfonic acids in question, is settled and separated from the oil. After the separation, the "acid jelly" is neutralized, and then, permitted to settle, whereby the neutralized mixture separates into three layers, viz., a top oil layer; a middle emulsion layer; and a lower aqueous layer, containing the mahogany sulfonates. The lower aqueous layer is carefully withdrawn, and, if desired, treated with naphtha to extract substantially all oil, and then mahogany sulfonates are salted out, yielding a product which consists of mahogany sulfonates and water with a minimum amount of oil and a minor amount of salt. Since the sulfo-

nates are to be used for breaking petroleum emulsions, the removal of oil is unnecessary, and therefore, the naphtha washing step may be eliminated.

We prefer to use the mahogany sulfonates as a sodium salt. However, it is to be understood that equivalent water soluble, oil insoluble salts or derivatives, including tri-ethanolamine salts, may be used. These particular mahogany sulfonates are excellent demulsifiers when used alone, however, they may be used, if desired, in combination with other demulsifiers, and in some instances, certain advantages are obtained by combinations of demulsifiers. A particularly effective combination is obtained by employing a mixture of the mahogany sulfonates and salts of naphthenic acids, such as sodium or ammonium naphthenates.

Our demulsifiers may be used as a water solution, or they may be used in solution in a suitable organic solvent, such as a light petroleum distillate solvent or an alcohol or a mixture of organic solvents. In this connection, it might be notel that solvent naphthas of high Kauri-Butanol values have been found to be particularly effective solvents for our demulsifiers. Further, the use of organic solvents of low-freezing points, such as naphthas and alcohols, has an advantage over the use of water in that freezing difficulties during cold weather are avoided.

vigorous shakes, and allowed to stand at room temperature (76° F.). Readings of the amount of clear water and of "B. S." (rag-layer) were made after 10 minutes and 45 minutes of standing. Then a sample (6.25 ml.) of the supernatant oil was removed from about the 50 ml. mark of each tube by means of a pipette, diluted with an equal volume of white gasoline and centrifuged at 1200 R. P. M. for 5 minutes. Readings of per cent water and B. S. in the centrifuged samples told how clean the oil was at the time the samples were taken.

A third reading of the condition of the mixing cylinders after standing a total of 90 minutes was recorded and a second sample of the oil layer then ground out for cleanliness. By referring to the tabulated results, it is readily apparent that the combination of this invention consistently gave the cleanest oil.

In the table below, the demulsifier is identified as relative parts of a water soluble, oil insoluble mahogany sulfonate (A) and a sulfonic acid (X, Y and Z). The acid Y corresponds to the sulfonate A, i. e., sulfonate A was prepared by neutralization of an acid substantially identical with acid Y. X refers to sulfonic acids which form oil-soluble petroleum sulfonates, while Z designates green sulfonic acids contained in acid sludge from the refining of petroleum distillates.

Test data on demulsifiers

Test No.	Demulsifier used	Treating ratio	Mixing cylinders after—						Grindout			
			10 min. @ 65° F.		45 min. @ 76° F.		90 min. @ 76° F.		5 min.		C	
			A		B		C		B			
			Percent H_2O	Percent BS	Percent H_2O	Percent BS	Percent H_2O	Percent BS	Percent H_2O	Percent BS	Percent H_2O	Percent BS
1	78A—22X	1:2000	11.5	0.8	12.9	0.1	13.1	0.1	2.0	0	1.4	0
2	75A—25Y	1:2000	8.0	1.0	13.8	0.2	14.0	0.1	0.8	0	0.6	0
3	75A—25Z	1:2000	13.3	0.05	13.8	0.1	14.0	0.05	1.6	0	1.0	0
4	78A—22X	1:4000	12.0	0.3	13.6	0.05	14.0	0.05	3.4	0	2.8	0
5	75A—25Y	1:4000	12.5	0.5	15.6	0.1	15.8	0.1	0.85	0	0.65	0
6	75A—25Z	1:4000	11.0	0.1	12.9	0.05	13.8	0.05	3.2	0	2.4	0
7	78A—22X	1:8000	8.0	0.2	9.8	0.1	11.1	0.1	6.4	0	4.4	0
8	75A—25Y	1:8000	12.0	0.5	14.3	0.05	14.8	0.05	1.6	0	1.0	0
9	75A—25Z	1:8000	6.0	----------	11.2	0.05	14.0	0.05	----------	----------	5.4	0

We have found that demulsifying properties of the sulfonates described above is greatly enhanced by use thereof in combination with sulfonic acids of the type from which the sulfonates are derived, that is, mahogany sulfonic acids whose salts are water soluble and oil insoluble. Preferably, the acid used is substantially the same as the acid from which the sulfonate is derived. The preferred mixtures may be prepared either by partial neutralization of a suitable sulfonic acid mixture or the sulfonic acids may be divided into two parts, one of which is neutralized and the two portions blended in desired proportiins after formation of sulfonates from one portion.

The advantages of the present invention are demonstrated by tests in breaking an Illinois crude emulsion at 66° F.

The tests were carried out in the following manner: accurately measured quantities of dilute solutions of the demulsifiers were pipetted into labelled, glass-stoppered, 100 ml. graduated mixing cylinders. Then, as rapidly as possible, all cylinders were filled to the 100 ml. mark by decantation from a large pitcher of the emulsion. The containers were stoppered, each given 50

We claim:

1. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a water soluble, oil insoluble mahogany sulfonate and a mahogany sulfonic acid which forms water soluble, oil insoluble mahogany sulfonates, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

2. The process of breaking petroleum emulsions of the water-in-oil-type, which comprises treating the emulsion with a mahogany sulfonic acid which forms water soluble, oil insoluble sulfonates and a water soluble sulfonate of said acid, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

3. A demulsifier for petroleum emulsions of the water-in-oil type which comprises a water soluble, oil insoluble mahogany sulfonate and a mahogany sulfonic acid which forms water soluble, oil insoluble mahogany sulfonates, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

4. A demulsifier for petroleum emulsions of the water-in-oil type which comprises a mahogany sulfonic acid which forms water soluble, oil insoluble sulfonates and a water soluble sulfonate of said acid, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

5. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a solution in an organic liquid solvent having a low freezing point of a water soluble, oil insoluble mahogany sulfonate and a mahogany sulfonic acid which forms water soluble, oil insoluble mahogany sulfonates, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

6. The process of breaking petroleum emulsions of the water-in-oil type which comprises treating the emulsion with a solution in an organic liquid solvent having a low freezing point of a mahogany sulfonic acid which forms water soluble, oil insoluble sulfonates and a water soluble sulfonate of said acid, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

7. A demulsifier for petroleum emulsions of the water-in-oil type which comprises a solution in an organic liquid solvent having a low freezing point of a water soluble, oil insoluble mahogany sulfonate and a mahogany sulfonic acid which forms water soluble, oil insoluble mahogany sulfonates, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

8. A demulsifier for petroleum emulsions of the water-in-oil type which comprises a solution in an organic liquid solvent having a low freezing point of a mahogany sulfonic acid which forms water soluble, oil insoluble sulfonates and a water soluble sulfonate of said acid, said acid being present in sufficient quantity relative to said sulfonate to substantially enhance the demulsifier effect of the latter.

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