Patented Apr. 20, 1943 2,317,050

# UNITED STATES PATENT OFFICE

2,317,050

## BREAKING PETROLEUM EMULSIONS

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No Drawing. Application May 3, 1941, Serial No. 391,708

6 Claims. (Cl. 252—333)

This invention relates to the demulsification of water-in-oil emulsions encountered in the petroleum industry. Such emulsions are well-known since they are conventionally encountered in the oil production fields, and as "bottom settlings" (B. S.), and so forth. As a result, these emulsions have been the subject of extensive demulsification research.

It is an object of our invention to provide a new effective means for breaking petroleum emulsions.

A more specific object is to afford the use of certain water-soluble petroleum sulfonates as demulsifiers.

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 the co-pending application, Serial No. 336,714, filed May 23, 1940, now U. S. Patent No. 2,266,084, granted 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 now have discovered that water soluble, oil insoluble salts or 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. Other desirable petroleum stocks from which to manufacture the sulfonates to be used in our invention comprise, as is disclosed in the above-mentioned Patent No. 2,266,084, petroleum solvent tars or extracts which are obtained as a by-product in solvent refining petroleum oils.

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 Universal viscosity at 100° F. | Sulphuric acid used in treat per bbl. of oil | Property of sodium sulphonate of sulphonic 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..... | .....do..... | 70 lbs. of 98% acid (added in a plurality of treats). | Do. |
| Do..... | 72 to 79 sec.. | 50 lbs. of 98% acid (added in a plurality of treats). | Do. |

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 substan-

tially all oil, and then the 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 sulfonates 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 triethanolamine 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 noted that solvent naphthas of high kauributanol 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.

In order to show the surprising superiority of the water soluble, oil insoluble mahogany sulfonates over water soluble, oil insoluble green acids or green sulfonates, a direct comparison on the same emulsion is shown below. A Californian crude emulsion was used for the comparison. This oil had a dry gravity of about 28° A. P. I. and contains about 72% B. S. and W. The effectiveness of the demulsifiers is taken as the per cent of total water separated, compared to the total water content of the wet crude.

Using a ratio of demulsifier to crude of 1 to 5,000, a temperature of 108° F., and a settling time of 60 minutes, the following results were obtained:

| Demulsifier | Percent of B. S. and W. resolved |
|---|---|
| Stock A: | |
| Water soluble, oil<br>Insoluble mahogany<br>Ammonium sulfonates | 100. |
| Water soluble, oil<br>Insoluble mahogany<br>Sodium sulfonates | 100. |
| Stock B: | |
| Water soluble, oil<br>Insoluble mahogany<br>Sodium sulfonates | Fully equivalent in operation to stock A water soluble, oil insoluble mahogany sodium sulfonates. |
| Stock B, green acids | 0. |
| Sodium<br>Salt | 30. |
| Ammonium<br>Salt | 0. |
| Stock C, green acids | 0. |
| Sodium<br>Salt | 49 |
| Ammonium<br>Salt | 0. |
| Stock D, green acids | 0. |
| Sodium<br>Salt | 74. |
| Ammonium<br>Salt | 0. |

The petroleum stocks from which the above sulfonic acids and sulfonates were derived are characterized by the following properties:

| Stock | Source | °A. P. I. gravity | S. U. V. @ 100° F. |
|---|---|---|---|
| A | Coastal | 25.7 | 55 secs. |
| B | do | 24.8 | 75 secs. |
| C | Mid-Continent | 35.1 | 95 secs. |
| D | Mid-Continent<br>Furfural extract | 23.9 | 105" @ 130° F. |

The very real and substantial advantage afforded by the use of water soluble, oil insoluble mahogany sulfonates is apparent from the above comparison.

In practice our demulsifiers may be employed in substantially the same amounts and in substantially the same manner as are now conventional and well-known for the use of other demulsifiers.

It also might be noted that the water soluble, oil insoluble mahogany sulfonates, with or without other agents, such as naphthenates, may be used in processes of the type set forth in De Groote Patent No. 1,892,205 for preventing clogging in well and pipe lines because of deposition of solid matter, such as wax, etc.

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.

2. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a petroleum sulfonate demulsifier composition which contains water soluble, oil insoluble mahogany sulfonates as the predominant type of petroleum sulfonates.

3. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a demulsifier composition, containing water soluble, oil insoluble mahogany sulfonates and naphthenic acid bodies of the class consisting of naphthenic acids and water soluble salts thereof as the predominant demulsifiers.

4. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a petroleum sulfonate demulsifier composition which contains water soluble, oil insoluble mahogany sulfonates, as the predominant type of petroleum sulfonates and which is characterized further by having the petroleum sulfonates dissolved in an organic liquid solvent of low-freezing point.

5. A demulsifier for breaking water-in-oil type petroleum emulsions comprising a solution of water soluble, oil insoluble mahogany sulfonates in a light organic liquid solvent of low-freezing point, said mahogany sulfonates being essentially the only type of petroleum sulfonates present.

6. The process of breaking petroleum emulsions of the water-in-oil type, which comprises treating the emulsion with a petroleum sulfonate demulsifier composition which contains water soluble, oil insoluble mahogany sulfonates, as the predominant type of petroleum sulfonates and which is characterized further by having the petroleum sulfonates dissolved in a light petroleum distillate solvent.

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