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TREATMENT OF PETROLEUM HYDROCARBON STOCKS

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This invention relates to the treatment of petroleum hydrocarbon stocks.

One object of the invention comprises, inter alia, the production of mahogany sulphonic acids from petroleum hydrocarbon stocks. Another object of the invention comprises, an improved procedure for the refining of petroleum hydrocarbon stocks in a manner yielding mahogany sulphonic acids in larger amounts than has been hitherto possible in accordance with conventional practices.

In accordance with the invention, a suitable petroleum hydrocarbon stock is sulphonated in the presence of a suitable organic solvent substantially freely miscible with such stock and having, relative to said stock, a preferential solvency for mahogany sulphonic acids to the substantial exclusion of green sulphonic acids. Within the preferred embodiment of my invention, the sulphonation is conducted with sulphuric acid under sulphonating conditions of acid concentration and temperature in a manner well known in the acid refining of petroleum hydrocarbon stocks as, for instance, lubricating oil distillates derived from petroleum. When using the sulphuric acid procedure, the organic solvent should be substantially non-reactable and substantially immiscible with the acid under the sulphonating conditions referred to.

A suitable petroleum hydrocarbon stock in accordance with my invention may be any sulphonatable petroleum hydrocarbon stock. Such petroleum hydrocarbon stock may be, for instance, one conventionally used for the production of refined petroleum distillates. In general, any raw petroleum hydrocarbon stock or partly refined petroleum hydrocarbon stock including solvent refined petroleum hydrocarbon stock may be used provided, however, that the same is sulphonatable.

In conventional acid refining practices, as, for instance, in the treatment of certain lubricating oil distillates, derived from petroleum, the refining treatment includes the application of sulphuric acid under sulphonating conditions. As a rule the acid used is fuming sulphuric acid. Though the concentration of SO_3 in the fuming acid may vary considerably, a 20% fuming acid is employed in the majority of cases. The acid application is regulated in a manner well known in the art to produce the desired sulphonation reaction and in general temperatures not exceeding 150°F. are preferred. As a result of the sulphonation obtained in the sulphuric acid treatment sulphonic acids are formed. These are

primarily of two kinds, i. e., the so-called "petroleum mahogany sulphonic acids," usually termed for brevity "mahogany sulphonic acids," remaining dissolved in the oil and the so-called "petroleum green sulphonic acids," usually termed for brevity "green sulphonic acids," predominantly found in the sludge and primarily of a water-soluble character. After the separation of the oil from the acid sludge the mahogany sulphonic acids may be recovered from the oil in the form of a more or less crude mahogany sulphonate stock in accordance with well-known procedures. This mahogany sulphonate stock constitutes a valuable product and as hereinabove stated, one of the objects of the invention involves, inter alia, a petroleum hydrocarbon stock refining treatment in which the yield of mahogany sulphonic acids is increased.

Within the preferred embodiment of my invention, I may utilize as a solvent an halogenated and preferably chlorinated aliphatic normally liquid hydrocarbon. Suitable solvents of this type are for instance the various chlorinated derivatives of methane, ethane, propane, butane, pentane, etc. I find it of advantage to use a solvent in which in addition to the characteristics herein specified possesses additionally, a vapor pressure and boiling point such that its use involves a minimum of vaporization losses and maximum ease of removal and solvent recovery. A solvent of this preferred type is for instance, amyl chloride.

As to the amount of solvent within the procedure of my invention, there is a direct functional relation between amount of solvent used and the yield of mahogany sulphonic acids. Such yield increases with increased amounts of solvent. The increase in yield of mahogany sulphonic acids becomes in most cases substantial at approximately 10% by weight of solvent calculated on the weight of petroleum stock under treatment and reaches its maximum at approximately 100% solvent, calculated on such stock. In some cases however substantial yield increases are obtained by relatively small amounts of solvent and satisfactory yield increases may thus be obtained with amounts of solvent as low as, for instance, 1% by weight of the stock. Amounts of solvent in excess of 100% do not seem to further appreciably increase the yield of mahogany sulphonic acids.

In the majority of cases, the sulphonation conditions employed may be those conventionally used in the acid refining of petroleum hydrocarbon stocks of the same descriptive properties as

are to be treated in accordance with my invention. The mahogany sulphonic acid yields, within the practical application of my invention, are materially higher than those ordinarily obtained when acid refining petroleum hydrocarbon stocks of the same or similar descriptive characteristics in the conventional manner.

When proceeding in accordance with the invention, the sulphonation reaction by way of sulphuric acid treatment is preferably conducted by adding the sulphuric acid in a multiple number of successive shots. Within the preferred practice, it is then advisable to withdraw the acid sludge formed after at least some of the shots, and to neutralize the remaining solvent-oil layers after at least some of the withdrawals. When proceeding in this manner, the mahogany sulphonic acid yield recovered by way of the sulphonates is still further enhanced. In the majority of cases, it is advisable to withdraw the sludge and neutralize after each shot. Satisfactory results are for instance obtained by adding the sulphuric acid in four successive shots, withdrawing the acid sludge after each shot and neutralizing the remaining solvent-oil layer after each such withdrawal.

The following Example I illustrates one embodiment of the invention:

EXAMPLE I

Five neutrals, respectively ranging in viscosity from 40 to approximately 500 seconds at 100° F. were treated. Each neutral was subjected to an acid treatment in the presence of an equal amount by weight of carbon tetrachloride by adding in succession in the usual manner four shots of oleum (20% SO₃ content), at a temperature of approximately 100 to 150° F., after each shot withdrawing the acid sludge formed, neutralizing the oil layer and recovering from the latter, after the removal of the solvent, preferably by way of distillation, mahogany sulphonates in accordance with conventional procedures.

The same stocks used in the foregoing Example I were each subjected to the same sulphonation treatment but without the presence of carbon tetrachloride. The respective mahogany sulphonic acid yields obtained for the various neutrals for both the conventional acid treatment without solvent as well as for the acid treatment in accordance with the invention in the presence of a solvent are shown by way of the sulphonate yields in the following table:

TABLE I
Comparison of yields

Stock (viscosity in seconds at 100° F.)	Per cent yield of mahogany sulphonates		Per cent increase by treating in presence of solvent
	Solvent absent	Solvent present	
500.....	10.7	22.0	105
150.....	6.0	14.0	133
100.....	2.3	6.2	170
60.....	1.4	4.8	242
40.....	0.1	0.4	300

The following Example II is furnished by way of demonstrating the mahogany sulphonic acid yield using different solvents in accordance with the invention as compared with the conventional procedure of acid refinement using no solvent:

EXAMPLE II

A 500 viscosity neutral is treated with three shots of 10% oleum, using the successive addition method, at a temperature of from 100 to 150° withdrawing the acid sludge after each shot and neutralizing the solvent-oil layer after each withdrawal. After the separation of the acid sludges, the oil layers were worked up in the usual manner for mahogany sulphonates. The same neutral was then treated in a series of runs in the same manner except that in each run the sulphonation was carried out in the presence of an equal amount by weight of solvent. The solvents used were methylene dichloride, chloroform, carbon tetrachloride, ethylene dichloride, and amyl chloride. In each case the ultimately resulting oil layers were worked up for mahogany sulphonate.

The yields of mahogany sulphonic acids obtained in the various runs of Example II are shown by way of the sulphonate yields in the following table:

TABLE II

Stock treated: 500 neutral with 3 10% shots oleum

Solvent used	Yield mahogany sulphonates
	Per cent
None.....	10.7
Methylene dichloride.....	24.4
Chloroform.....	23.4
Carbon tetrachloride.....	22.0
Ethylene dichloride.....	24.8
Amyl chloride.....	25.4

It will be seen from the foregoing table that in each case when the sulphonation was carried out in the presence of a solvent, as compared with the run when the sulphonation was carried out without solvent under otherwise identical conditions, the mahogany sulphonate yield was more than twice that of the blank run.

In the recovery of mahogany sulphonic acids by way of their sulphonates in accordance with conventional procedure, the sulphonates are as a rule recovered in the form of a more or less crude stock usually containing occluded hydrocarbon material, in some cases up to 40% and even higher. When reference is made herein to the expression "mahogany sulphonates," or such similar expression, the same is intended to include a sulphonate product irrespective of whether the same contains occluded oil or not.

Where reference is made herein to "sulphuric acid," such expression is used generically and is intended to include, as is well understood in the art, fuming sulphuric acid or oleum.

The foregoing description is by way of illustration and not of limitation, and it is, therefore, my intention that the invention be limited only by the appended claims or their equivalent, wherein I have endeavored to claim broadly all inherent novelty.

I claim:

1. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement comprising sulphonating such stock with fuming sulfuric acid in the presence of a chlorinated aliphatic normally liquid hydrocarbon.

2. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement in accordance with claim 1 in which said chlorinated aliphatic hydrocarbon is present in amount equal

to at least approximately 10% by weight calculated on the weight of said stock.

3. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement in accordance with claim 1 in which said chlorinated aliphatic hydrocarbon is present in amount equivalent to approximately in equal weight calculated on the weight of said stock.

4. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement comprising sulphonating said stock with fuming sulfuric acid in the presence of at least 10% by weight, calculated on the weight of said stock of an aliphatic chlorinated normally liquid hydrocarbon of the methane to pentane series.

5. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement in accordance with claim 4 in which said chlorinated aliphatic hydrocarbon is amyl chloride.

6. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement comprising sulphonating such stock with a number of successive shots of fuming sulphuric acid in the presence of at least approximately 10% by weight calculated on the weight of said stock, of a chlorinated aliphatic normally liquid hydrocarbon of the methane to pentane series, withdrawing the acid sludge formed after at least some of said shots, neutralizing the remaining solvent-oil phases after at least some of said withdrawals and recovering mahogany sulphonates from said solvent-oil phases.

7. In the treatment of a sulphonatable petroleum hydrocarbon stock, the improvement in accordance with claim 6 in which said stock is a sulphonatable raffinate derived from the solvent refining of a petroleum hydrocarbon stock.

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