Sept. 13, 1955 L. P. HODGES 2,717,879

RECOVERY OF TREATING SOLUTION

Filed Dec. 17, 1952 2 Sheets-Sheet 1

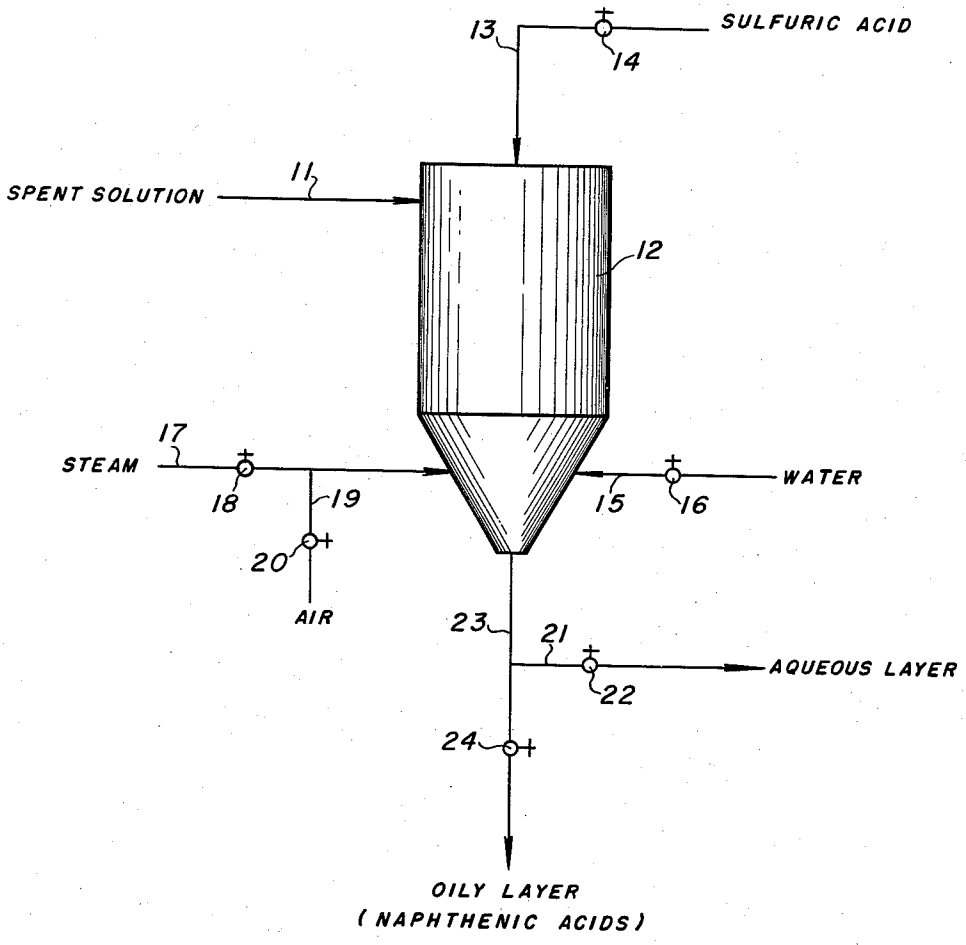


FIG. 1.

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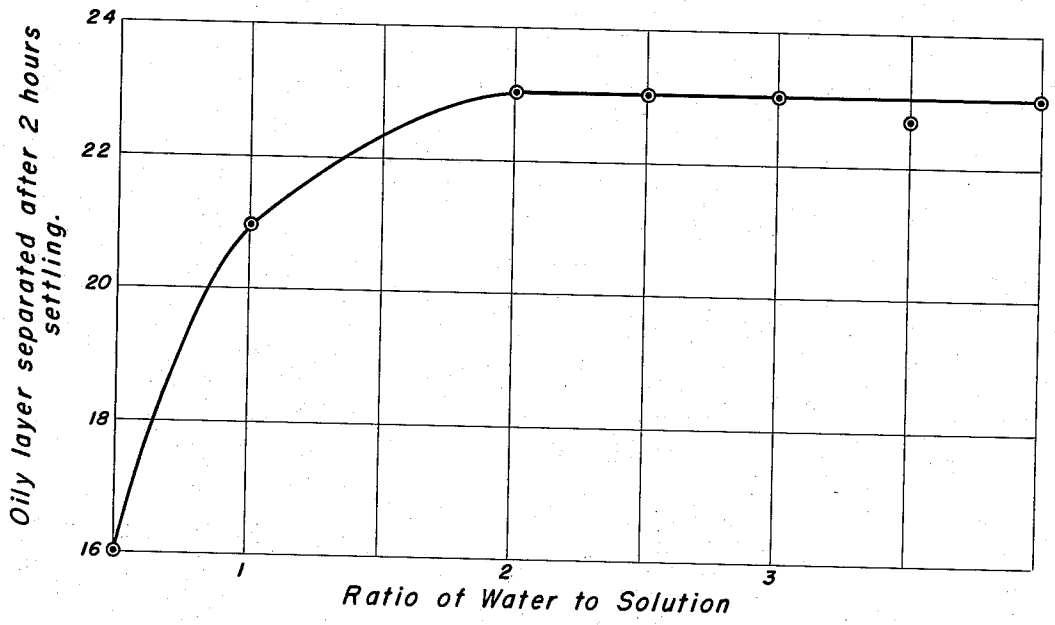
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FIG. 2.



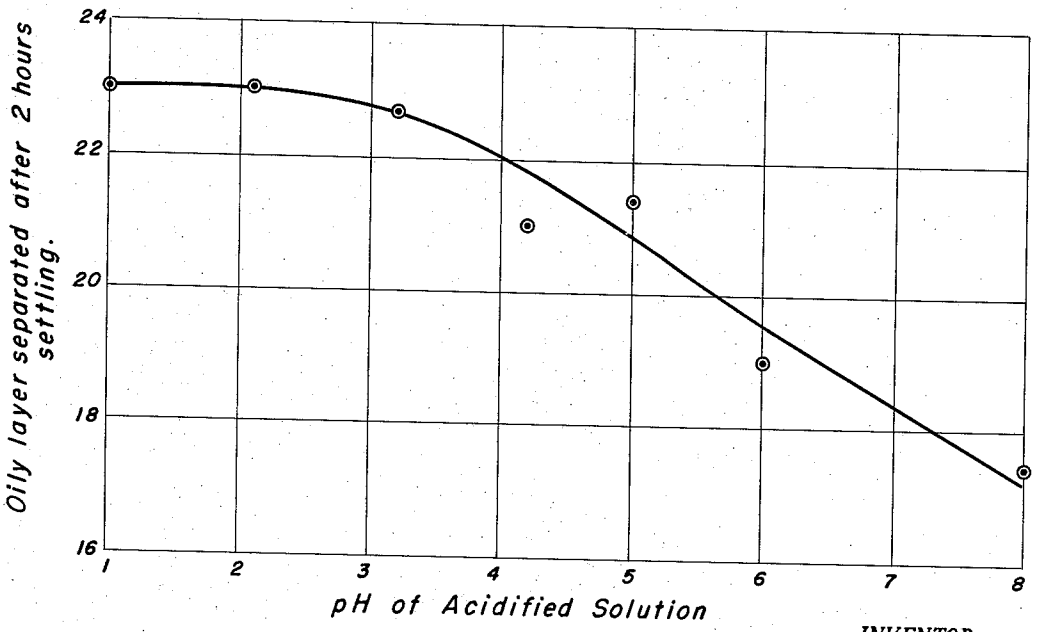


FIG. 3.

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RECOVERY OF TREATING SOLUTION

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Application December 17, 1952, Serial No. 326,551

7 Claims. (Cl. 252—182)

The present invention is directed to a method for recovering a treating solution. More particularly, the invention is directed to the recovery of a treating solution from an aqueous solution containing naphthenic acid salts.

The present invention may be briefly described as involving the treatment of an aqueous solution containing naphthenic acid salts in admixture with sulfonic acid salts, alkali metal sulfates, free alkali metal hydroxide, and a small quantity of entrained oil by diluting the solution with water, acidifying the diluted solution with a mineral acid, settling the acidified solution to form an aqueous layer and an oily layer and recovering the naphthenic acids from the oily layer. The treating agent is recovered from the aqueous layer.

The naphthenic acids are separated in the present invention from a solution containing naphthenic acid salts, such as alkali metal naphthenates, aryl sulfonic acid salts, alkali metal sulfates, free alkali, entrained oil, and water. This solution is obtained by treating lubricating oil fractions and the like containing naphthenic acids, such as a Coastal lubricating oil fraction and lubricating oils from California type crudes, with a treating reagent comprised of sodium aryl sulfonates, sodium sulfate, free sodium hydroxide, and water. This treating reagent is conveniently obtained by treating with an alkali, such as sodium hydroxide, a sulfuric acid treated aromatic fraction. For example, the treating reagent, which is employed to treat lubricating oil fractions to remove naphthenic acids from them, may be obtained in a process such as described by Schutze in U. S. Patent 2,400,373. In short, the spent caustic solution withdrawn in the aforesaid Schutze patent is admirable as a treating reagent for removing naphthenic acids from naphthenic acids containing lubricating oil fractions and it is the solution resulting from treating lubricating oil fractions containing naphthenic acids with the spent caustic of the aforesaid Schutze patent that I employ as a feed stock.

The treating reagent employed in the practice of the present invention before use in treating lubricating oil should contain amounts of the several components thereof in the range of

Table I

	Per cent
Alkali metal hydroxide	0.5–5
Alkali metal salt of sulfonic acid	10–30
Alkali metal salt of inorganic acid	5–10
Water	55–84.5

The solution of the treating reagent should have a specific gravity no less than 1.10.

The spent aqueous solution is comprised of alkali metal naphthenates, alkali metal aryl sulfonates, alkali metal sulfates, alkali metal hydroxide and entrained oil. Inspections of two of such solutions are shown in the following table:

Table II

Inspections	Solution I	Solution II
Specific Gravity	1.15	1.11
Oil Content, Wt. Percent	0.8	10.8
Naphthenates and Sulfonates, Wt. Percent	27.6	13.3
Sodium Sulfate, Wt. Percent	9.2	11.4
Free NaOH, Wt. Percent	3.6	0.7
Water (By Difference), Wt. Percent	58.8	63.8

Solution I is the preferred solution.

The amount of water employed in the present invention should be a sufficient amount to dilute the solution with no less than 2 volumes of water per volume of solution. If less than 2 volumes of water per volume of solution are employed, the benefits of the present invention are not achieved in that the naphthenic acids and the oil entrained with the solution on acidification will not completely separate from the solution and oil and naphthenic acids will be lost. The water may be preferably added to the solution prior to the subsequent acidification, as will be described. It is desirable to admix the water with the solution intimately to achieve good contact.

The amount of acid employed in my invention is sufficient to produce a pH no greater than 3 in the aqueous layer. If lesser quantities of acid are added to give a pH greater than 3 the benefits of my invention are not realized since the naphthenic acids and oil remain in admixture with the aqueous phase.

Any mineral acid may be used, such as sulfuric acid or hydrochloric acid. However, it is preferred to use sulfuric acid having a Bé. gravity in the range from about 25° to 30°. Sulfuric acid available in the modern petroleum refinery, such as acid which has been used in treating petroleum fractions, is entirely suitable in my invention. The acid should be intimately mixed with the solution by a suitable means. Stirring or agitating with steam or air may be used. The use of air for agitation is preferred.

Temperature is not critical in the practice of my invention. It may range from ambient temperature in the Gulf Coast area to 210° F. It is preferred to use a temperature in the range from 170° to 190° F.

The present invention may be briefly described by reference to the drawing in which Fig. 1 illustrates a preferred mode of practicing the invention;

Fig. 2 is a plot of data illustrating the effect of dilution with critical amounts of water; and

Fig. 3 is a plot of data similar to Fig. 2 illustrating the effect of controlled acidity.

Referring now to the drawing and particularly to Fig. 1, numeral **11** designates a charge line through which the spent solution is discharged into kettle **12**. Kettle **12** is provided with line **13** controlled by valve **14** through which sulfuric acid may be introduced and line **15** controlled by valve **16** through which water may be introduced. The kettle **12** has a line **17** controlled by valve **18** arranged to discharge steam into kettle **12** at a lower portion therein. Line **19** controlled by valve **20** ties into line **17** and allows line **17** to be used for introduction of air into kettle **12** as will be described further. Line **21** equipped with valve **22** connects into line **23** and these lines serve for removal of the two phases from kettle **12** as will be described. Line **23** is controlled by valve **24**.

In practicing the process of my invention, the spent solution is pumped through line **11** into kettle **12**. Water at a temperature in the range from 170° to 210° F. is

pumped into kettle **12** through line **15** until at least two volumes of water have been added for every volume of spent solution in the kettle. Air is then discharged from line **19** into line **17** and thence into the kettle **12**, valve **18** remaining in the closed position. This air is discharged into the kettle **12** for 2 to 3 minutes to thoroughly mix the contents thereof. After the water and spent solution are thoroughly mixed, valve **20** is closed to shut off the supply of air and sulfuric acid is introduced through line **13** in a quantity sufficient to produce an acidified solution having a pH no greater than 3. The flow of sulfuric acid to the kettle **12** is terminated by closing valve **14**. The mixture is then thoroughly stirred by air blowing for 2 to 3 minutes in the manner previously described. The contents of kettle **12** are allowed to settle for about 1 hour. After settling for about an hour, valve **22** is opened and the aqueous layer is withdrawn through line **21**, valve **24** being maintained in the shut position, and the aqueous layer is passed to a suitable recovery system. After the aqueous layer has been removed, valve **22** is closed and valve **24** is opened so that the oily layer containing the naphthenic acids may be discharged through line **23** into suitable storage. The percentage of oil in the naphthenic acid is small.

It will be seen from the foregoing description taken with the drawing that beneficial results flow from diluting the naphthenic acid salt solution with controlled amounts of water and acidifying thereafter to a controlled pH.

In order to illustrate the benefits to be derived by the dilution of the spent solution in accordance with my invention, 8 equal portions of the spent solution were stirred with varying quantities of water and allowed, after acidifying to a pH of 2, to settle for 2 hours. The volume of the oily layer was measured for each portion. The results of these runs along with the amounts of solution, water, and the ratio of water to solution are presented in Table III:

Table III

Volume Solution	Volume H_2O	pH	Ratio H_2O:Solution	Oily Layer after 2 Hours, Percent
200	100	2	½:1	16
200	200	2	1:1	21
200	300	2	1½:1	21.5
200	400	2	2:1	23.0
200	500	2	2½:1	23.0
200	600	2	3:1	23.0
200	700	2	3½:1	22.7
200	800	2	4:1	23.0

A plot of these data is shown in Fig. 2.

It is apparent from these data and Fig. 2 that the maximum yield of the oily layer is obtained when employing a ratio of water to solution at a constant pH below 3 greater than 2:1. Although not reflected directly by the data, the clean separation of oily layer indicates a clean break between the oily layer and the aqueous layer, elimination of emulsion difficulties and recovery of substantially all of the oil and naphthenic acids.

The benefits to be derived by acidifying the diluted solution to a pH no greater than 3 will now be illustrated. A number of runs were made by taking equal quantities of the spent solution, diluting each of these quantities with 3 times its volume of water and acidifying with sulfuric acid. The amount of acid added to each portion was different so that pH values in the range from 1 to 8 were obtained. The portions were thoroughly stirred and allowed to settle for 2 hours after which time the volume of oil obtained from each portion was measured. These data are shown in the following table IV and a plot of the data are presented as Fig. 3.

Table IV

Volume Solution	Volume H_2O	pH	Oily Layer After 2 Hours, Percent
100	300	1	23.0
100	300	2.1	23.0
100	300	3.2	22.7
100	300	4.2	21.0
100	300	5.0	21.2
100	300	6.0	19.0
100	300	8.0	17.5

It is apparent from the data in Table IV and Fig. 3 that acidification to a pH greater than 3 results in lesser quantities of the oily layer being liberated; thus the full benefits of my invention are derived only by acidification to a pH no greater than 3 and by dilution with at least 2 volumes of water per volume of solution as reflected by the data in Tables III and IV and Figs. 2 and 3.

The oily layer consists of naphthenic acids containing small quantities of entrained oil. These naphthenic acids are sufficiently pure for most purposes. If so desired, the naphthenic acids may be further purified by any of several well known procedures such as extraction with alcohol, steam distillation, and the like.

The sulfonic acids which are released in this process are water soluble and remain in the aqueous layer. This aqueous layer may be concentrated by some suitable means such as distillation and then made caustic by the addition of an excess at least 0.5% of an alkali metal hydroxide to obtain a treating agent suitable for use in the practice of my invention.

The aqueous treating solution comprising alkali metal naphthenates, alkali metal aryl sulfonates, alkali metal sulfates, and alkali metal hydroxide may contain any of the alkali metals such as sodium, potassium, lithium, or the like. Sodium is the preferred alkali metal.

The naphthenic acids recovered in the practice of the present invention may suitably be used in the manufacture of paint driers and chemical intermediates. They may also be used in the manufacture of superior emulsifying agents. Since naphthenic acids are much in demand, my invention allows increased recovery of these materials from solution in petroleum refinery by-products from whence they ordinarily might be lost.

Although the invention has been described and illustrated by examples in which the solution after acidification was settled for 1 to 2 hours, it is within the scope of my invention to employ shorter and longer settling times. For example, under some conditions it may be desirable to settle for as little as 30 minutes, but under other conditions as much as 6 hours may be required.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for treating an aqueous solution containing alkali metal naphthenates, alkali metal sulfonates, alkali metal sulfates, alkali metal hydroxide and oil to recover said solution and separate naphthenic acids which comprises diluting said solution with no less than 2 volumes of water per volume of solution and then acidifying said diluted solution with a mineral acid in an amount sufficient to provide an acidified solution having a pH no greater than 3, settling the acidified solution to form an aqueous layer and an oily layer, recovering said oily layer containing naphthenic acids, and concentrating and neutralizing said aqueous layer to provide a treating reagent comprising alkali metal hydroxide, alkali metal salt of sulfonic acid, alkali metal salt of inorganic acid, and water in amounts, respectively, in the range between 0.5% and 5% by weight, 10% and 30% by weight, 5% and 10% by weight, and 55% and 84.5% by weight.

2. A method in accordance with claim 1 in which the mineral acid is sulfuric acid.

3. A method in accordance with claim 2 in which the sulfuric acid is a sulfuric acid which has been used in refining petroleum fractions.

4. A method for treating an aqueous solution containing sodium naphthenates, sodium aryl sulfonates, sodium sulfates, sodium hydroxide, and oil to recover said solution and separate naphthenic acids which comprises diluting the solution with no less than 2 volumes of water per volume of solution at a temperature in the range from 170° to 210° F., admixing and then acidifying said diluted solution with sulfuric acid having a Bé. gravity in the range from about 25° to 30° F. to provide an acidified solution having a pH no greater than 3, settling the acidified solution for a time in the range of about 30 minutes to about 6 hours to form an aqueous layer and an oily layer, recovering the aqueous layer, separating naphthenic acids from said oily layer, and concentrating and neutralizing said aqueous layer to provide a treating reagent comprising sodium hydroxide, sodium aryl sulfonates, sodium sulfates and water in amoutns, respectively, in the range between 0.5% and 5% by weight, 10% and 30% by weight, 5% and 10% by weight, and 55% and 84.5% by weight.

5. A method for the recovery of an aqueous treating solution comprising alkali metal sulfonates, alkali metal sulfates, and an alkali metal hydroxide and naphthenic acids from an aqueous mixture containing alkali metal naphthenates, alkali metal sulfonates, alkali metal sulfates, alkali metal hydroxide and oil which comprises diluting said mixture with at least 2 volumes of water per volume of mixture, acidifying said diluted mixture with a mineral acid in an amount sufficient to provide an acidified mixture having a pH no greater than 3, settling the acidified mixture to form an aqueous layer and an oily layer, separating the layers, neutralizing said separated aqueous layer with an alkali metal hydroxide, adding an excess of at least 0.5% of an alkali metal hydroxide to the neutralized solution and concentrating said aqueous layer to a specific gravity of no less than 1.10 to obtain a treating reagent comprising alkali metal hydroxide, alkali metal salt of sulfonic acid, alkali metal sulfate and water in amounts, respectively, in the range between 0.5% and 5% by weight, 10% and 30% by weight, 5% and 10% by weight, and 55% and 84.5% by weight.

6. A method in accordance with claim 5 in which the mineral acid is sulfuric acid.

7. A method in accordance with claim 5 in which the alkali metal is sodium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,072,053	Hendrey	Feb. 23, 1937
2,170,506	Reiber	Aug. 22, 1939
2,477,190	Linford et al.	July 26, 1949
2,481,570	Champegnot	Sept. 13, 1949
2,537,576	Dunlap	Jan. 9, 1951
2,685,558	Hodges	Aug. 3, 1954