Patented Sept. 29, 1942

2,297,621

UNITED STATES PATENT OFFICE

2,297,621

METHOD FOR REMOVING ACIDIC SUBSTANCES FROM LIQUID HYDROCARBONS

Lawrence M. Henderson, Winnetka, and George W. Ayers, Jr., Chicago, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application April 17, 1941, Serial No. 388,982

12 Claims. (Cl. 196—30)

This invention relates to a method of removing acidic bodies from water immiscible liquids and to a reagent for accomplishing the same. More particularly, the invention is directed to the problem of removing sulfur compounds from hydrocarbon oils.

This application is a continuation in part of application, Serial No. 341,904, filed June 22, 1940, in the names of Lawrence M. Henderson and George W. Ayers, Jr.

Hydrocarbon oils, particularly light distillates resulting from cracking higher boiling fractions frequently contain mercaptans and other acidic sulfur compounds which require removal in order to render the oil "sweet" and non-corrosive. It has been common practice in the petroleum refining art to remove part of the sulfur compounds by washing with caustic alkali and then to sweeten with doctor solution. The disadvantage involved in this type of treatment is that a considerable portion of the sulfur remains in the oil or distillate and adversely affects the anti-knock properties of the gasoline. Gasoline containing sulfur compounds such as organic disulfides, usually not only has a lower octane rating than substantially sulfur-free gasoline, but requires much more tetra-ethyl lead to raise its octane rating to a given value.

More recently an improvement in caustic washing for removal of mercaptans and other sulfur compounds has been effected by adding to the caustic solution materials such as sodium or potassium isobutyrate, commonly known as "solutizers" or solubility promoters.

We have discovered that the results obtained by washing with caustic alkali solution either alone or containing commercially known solubility promoters can be considerably improved upon by adding to caustic alkali solution of fairly high concentration a soap or acid, the solubility of which in the alkali solution is low, and a solventizer therefor, i. e., a substance which will enable larger quantities of the soap or acid to dissolve in the caustic solution.

Caustic alkali solutions of fairly high concentration will dissolve only relatively small quantities of acid or soap such as naphthenic acids or alicyclic carboxylic acids and the soaps thereof, and in the quantities that the soap or acid is dissolved in the caustic alkali it has no material effect insofar as enhancing the ability of the caustic solution to remove acidic substances such as mercaptans and thiophenols from hydrocarbon oils However, if a material is added having the ability to increase the solubility of the soap or acid in the caustic alkali and a sufficient amount of soap or acid is added to the caustic solution, the ability of the caustic to remove mercaptans and other sulfur compounds is greatly enhanced.

On the other hand, caustic alkali solutions of low concentrations will dissolve relatively large amounts of naphthenic or other acids and their soaps, but in low concentrations the caustic alkali solution per se or with addition of the acid or soap is relatively ineffective in removing mercaptans from the oil. If an attempt is made to increase the concentration of the caustic to a point where it is fairly effective in removing mercaptans, the naphthenic acid or other acid soap precipitates out of solution.

A number of different compounds have been found to be useful as solventizers. These compounds also have merit per se as solubility promoters. Included among such compounds are glycols such as ethylene glycol, phenols including phenol, o-, m- and p-ethyl phenol, normally liquid xylenols and mixtures thereof, cresols, 2,3,5-trimethylphenol, butylpyragallol, 3,4 dihydroxydiphenyl, p-chlor-m-cresol, alpha-naphthol, thiophenols such as thiophenol, o- and m-tiocresol, chlorphenols such as o- and p-chlorphenol and 2,4,5 trichlorphenol. The solventizers must be soluble in the resulting solution to the extent of at least 2% by weight of the solution. In order to realize to an appreciable extent the benefits of the invention, the solution should contain at least 5% by weight of free alkali metal hydroxide, preferably sodium or potassium hydroxide, that is alkali metal hydroxide in excess

of the amount required to stoichiometrically react with all solventizers present and all materials added as solubility promoters. Thus, irrespective of whether the solventizers and solubility promoters are added to alkali solutions in acidic form or as the alkali metal reaction products thereof, the finished treating solutions are considered to be alkali metal hydroxide solutions containing the alkali metal reaction products of the materials employed as solventizers and solubility promoters. The solubility promoters are preferably employed in amounts ranging from 10%, calculated in terms of the acidic form of the material, of the alkali solution up to an amount corresponding to the maximum amount of soap soluble in the alkali solution, although it is preferred to use an amount not over approximately 90% of the maximum amount soluble. The amount of solventizers may vary with the particular solventizer used and particular solubility promoter employed and may be as low as 2% by weight of the caustic alkali solution and as much as the maximum amount soluble in the alkali solution. In general it is preferred to use quantities ranging from about 5% to 40% by weight of the solution. It is preferred that in no case shall the amount exceed about 90% of the maximum amount soluble in the solution. The ratio by weight of dissolved solventizer to solubility promoter is ordinarily about 1:1 to 1:3 for maximum solubility of solubility promoter.

The acidic materials and/or the alkali metal reaction products thereof which have been found to be particularly effective are the naphthenic acids and their alkali metal soaps. By the term "naphthenic acids" it is intended to include all alicyclic acids particularly those which occur naturally in crude petroleum and which are predominantly cyclic in structure such as carboxylic acids of cyclopentane and cyclohexane ring structure. These acids, generally speaking, fall within the empirical formulae $C_nH_{2n-1}COOH$, $C_nH_{2n-3}COOH$ and $C_nH_{2n-5}COOH$ and contain a cyclo-paraffinic ring having a carboxyl group attached to carbon in the ring or to an aliphatic chain which is in turn attached to carbon in the ring. The acids may be mono or poly cyclic, usually the former. An increase in the length of the aliphatic chain or in the number of aliphatic group substituents increases the tendency of the acids to behave as aliphatic acids. Since soaps of aliphatic acids, even those of as low molecular weight as heptylic acid, are too insoluble in sodium hydroxide solution to possess substantial merit as mercaptan solubility promoters, it is not desirable to have too many aliphatic carbon atoms per molecule present because of the concomitant low solubility. It is accordingly preferred to use those naphthenic acids which have at least a definite minimum solubility in aqueous alkali solution. Acids which have this alkali solubility are those acids which dissolve substantially completely to the extent of 18.7 pounds in a solution consisting of 18.3 pounds of sodium hydroxide, 6.3 pounds of commercial 5° cresol and 56.7 pounds of water at temperatures of about 70° F. It is apparent that in applying this solubility test to compositions containing mixtures of naphthenic acids of varying molecular weight and structure, that some of the acids may dissolve and others remain undissolved. If the dissolved acids are soluble to the aforementioned extent, they are alkali-soluble within the meaning of this invention. Naphthenic acids containing over about 8 or 9 carbon atoms per molecule, such as those containing between about 11 and 16 carbon atoms, are particularly effective. The naphthenic acids are especially useful if it is desired to use sodium hydroxide solution which ordinarily is the cheapest of the available strong bases since the naphthenic acids have been found to have considerably greater solubility in sodium hydroxide solutions than aliphatic acids of a corresponding number of carbon atoms. In fact, the solubility of the aliphatic acid soaps containing 7 or more carbon atoms per molecule in sodium hydroxide solution is so limited as to preclude the use of such soaps as solubility promoters. This is clearly demonstrated by the data in Table I.

Table I

Treating solution	Percent mercaptan sulfur in untreated gasoline	Percent mercaptan sulfur removed
(1) 15% NaOH	0.0260	47
(2) 15% NaOH, free 0.5% n-heptylic acid* 0.5% commercial cresol*	0.0260	48
(3) 15% NaOH, free 0.5% commercial cresol*	0.0260	48
(4) 15% NaOH	0.0265	51
(5) 10.55% NaOH, free 12% commercial cresol* 15% cyclohexanecarboxyic acid*	0.0265	72

*Present as sodium salts.

In each of the foregoing treating solutions except (5) there is 15 percent by weight free sodium hydroxide, i. e., sodium hydroxide in excess of that amount required to combine stoichiometrically with the cresol and acidic constituents present. In solution (5) the free sodium hydroxide is 10.55% by weight. In each case samples of sour gasoline were contacted for 5 minutes with 7 percent by volume of the treating solutions under an atmosphere of nitrogen. Solution 2 represents the most concentrated solution of sodium n-heptylate that it was possible to prepare using 15 percent by weight free sodium hydroxide and an amount of commercial cresol approximately equal to that of the heptylic acid radical employed. Solutions containing 15 percent by weight free sodium hydroxide, 2 percent by weight n-heptylic acid and 2 percent by weight of commercial cresol were prepared but these solutions gelled in a very short time and, therefore, could not be used as treating reagents.

It is apparent from the results shown in Table I that only a very small amount of n-heptylic acid can be dissolved in 15 percent sodium hydroxide solution even when using an equal amount of solventizer and that in the quantity that it is soluble, there is no increase in the mercaptan-extracting efficiency of the solution. When using 15 percent by weight of a naphthenic acid of an equivalent number of carbon atoms, (cyclohexanecarboxylic acid) a solution is readily formed although the amount of solventizer is appreciably less than the amount of acid. Furthermore, this solution (solution 5) is an excellent mercaptan-extracting solution as shown by the fact that in one application it removed 72 percent by weight of the mercaptan sulfur originally present in the gasoline.

A large number of tests were carried out using three samples of commercial naphthenic acids supplied by Socony-Vacuum Oil Company. These

acids are fully refined and have the properties shown in Table II. The data on "Apparent molecular weight" and "Formula" are taken from a booklet put out by the supplier, entitled "Socony-Vacuum Naphthenic Acids."

Table II

	1	2	3
A. P. I. gravity at 60° F	14.0	14.8	12.8
Neutralization No. (Mg. KOH per g.)	290/310	240/260	230/235
I. B. P	420	260	516
10%	475	490	528
20%	489	504	544
30%	494	516	558
40%	502	526	572
50%	512	540	588
60%	525	554	604
70%	540	568	618
80%	560	590	
90%	610	622	
E. P	615	624	
Per cent recovered	97.0	97.0	
78%			*622
Apparent molecular weight	188	218	249
Approximate formula	$C_{11}H_{20}O_2$	$C_{13}H_{24}O_2$	$C_{16}H_{28}O_2$

*Cracking.

An attempt was made to prepare an aqueous solution of 50% of naphthenic acid in caustic soda solution of such concentration of caustic that the resulting solution would contain 14.6% of free sodium hydroxide as determined by titration to phenolphthalein end point, using each of the three naphthenic acids above mentioned. A large part of the naphthenic acid salt precipitated out of solution as the sodium salt so that in no case did the resulting solution contain as high as 8% of sodium naphthenate calculated as naphthenic acid. The same experience was encountered in an attempt to prepare caustic potash solutions. On the other hand, when a small amount of phenol or m-cresol or corresponding thio compound was added to the caustic alkali solution, a solution containing 20% to 25% of naphthenate calculated as naphthenic acid was prepared with great ease.

The following table gives the results obtained by treating gasoline prepared by high pressure thermal cracking of a mixture of oil from Van Zandt and Schuler crudes. In the following table, "free NaOH" and "free KOH" represent NaOH or KOH present in the solution in excess of the stoichiometric amount required for combination with the acidic materials present.

Table III

Sample No.	Treating agent (aqueous solutions)	Per cent mercaptan sulfur in gasoline before treatment	Per cent mercaptan sulfur in gasoline after one wash with 10 per cent of treating solution	Per cent mercaptan sulfur removed
1	Caustic soda solution containing 0.77% by weight of NaOH	0.0233	0.0168	28
2	Caustic soda solution containing 0.77% free NaOH, 25% naphthenic acid, sample #3 (as sodium salt)	0.0233	0.0186	20
3	Caustic soda solution containing 14.6% by weight of NaOH	0.0267	0.0116	57
4	Caustic soda solution containing 11.0% by weight free NaOH, 8.4% by weight phenol, 25% by weight naphthenic acid (1) (as sodium salt)	0.0267	0.0051	81
5	Caustic soda solution containing 11.0% by weight free NaOH, 8.4% by weight phenol, 25% by weight naphthenic acid (2) (as sodium salt)	0.0267	0.0048	82
6	Caustic soda solution containing 11.0% by weight free NaOH, 8.3% by weight phenol, 25% by weight naphthenic acid (3) (as sodium salt)	0.0267	0.0044	84
7	Caustic soda solution containing 9.1% by weight free NaOH, 13.0% by weight naphthenic acid (1), 13.0% by weight phenol	0.0252	0.0067	73
8	Caustic soda solution containing 13.4% by weight free NaOH, 2.9% by weight phenol, 20.3% by weight naphthenic acid (1)	0.0252	0.0058	77
9	Caustic potash solution containing 20.5% by weight KOH	0.0262	0.0106	60
10	Caustic potash solution containing 15.5% by weight free KOH, 8.3% by weight phenol, 25% by weight naphthenic acid (1) (as potassium salt)	0.0262	*0.0009	97
11	Caustic soda solution containing 11.0% by weight free NaOH, 8.3% by weight m-cresol, 25% by weight naphthenic acid (1) (as sodium salt)	0.0262	0.0027	90

*Gasoline only slightly doctor sour.

Sample #10 was given a second treatment with 10% by volume of fresh treating solution followed by two 10% by volume water washes. The mercaptan sulfur after the second wash was only 0.0002% and the gasoline was sweet to the doctor test.

In each of the foregoing tests the gasoline was shaken with the treating solution for a period of fifteen minutes and then washed with two 10% by volume water washes.

The foregoing results clearly show that the dilute caustic alkali either alone or in which has been dissolved only naphthenic acid is relatively ineffective to remove mercaptan sulfur from cracked gasoline and that the effectiveness of caustic alkali solution of 14.6% NaOH was greater than that of the 0.77% caustic solution. Furthermore, caustic potash used in conjunction with the naphthenic acid soaps and solventizer is more effective than caustic soda. The results further show that with increasing amounts of naphthenic acids in more concentrated caustic alkali solution, the ability of the solution to remove mercaptans increases.

In order to determine the efficacy of the thiophenols in combination with soaps such as those of naphthenic acids in caustic solution a reagent was made by dissolving 20% of naphthenic acid (1) together with 6.7% o-thiocresol in a caustic soda solution, the free NaOH concentration of which was 14.6% by weight after addition of the naphthenic acid and thiocresol. This solution sweetened a sample of cracked gasoline contain-

ing 0.0213% mercaptan sulfur prepared from a mixture of Van Zandt and Schuler crudes with one 10% by volume treatment. When the same gasoline was treated with the same volume of a 14.6% caustic soda solution, only 57% of the mercaptan sulfur present in the gasoline was removed and the gasoline was distinctly sour.

Another reagent was prepared by dissolving 10% of o-thiocresol, 10% of m-cresol, and 20% of naphthenic acid (1) in caustic soda solution containing 10.7% free NaOH, and Stoddard Solvent, containing 0.0372% of mercaptan sulfur, fractionated from Illinois crude, was treated with the solution. The mercaptan sulfur was lowered to .001% whereas the treatment of the same Stoddard Solvent with straight caustic soda solution containing 14.6% caustic soda removed only 8% of the mercaptan sulfur present. Thus it will be seen that naphthenic acids or soaps thereof when used with solventizers such as the thiophenols which are in themselves effective agents in caustic solution for removing mercaptans have a much greater ability to remove mercaptans than naphthenic acids in the presence of solventizers which of themselves have little or no effect on mercaptan removal.

Particularly effective results were obtained with the following reagents shown in Table IV.

Table IV

	Treating agent (aqueous solution)	Percent mercaptan sulfur in original gasoline	Percent mercaptan sulfur removed
A	18.3% NaOH, total 18.7% naphthenic acid* 6.3% commercial cresol	0.0147	53
G	25% NaOH, total 12.5% naphthenic acid* 12.5% commercial cresol	0.0147	70
F	22.5% NaOH, total 15% naphthenic acid* 10% commercial cresol	0.0147	64

*Naphthenic acid marked *cc*-138B from Harshaw Chemical Company.

In each of the examples shown in Table IV, samples of gasoline were shaken for 5 minutes with 7% by volume of the treating agent in an atmosphere of nitrogen. While the proportions of mercaptans removed are not as high as on some other examples shown, it is probable that the difference is largely accounted for by differences in the characteristics of the gasoline treated.

It will be apparent that in preparing treating reagents in accordance with the invention, the solventizers may be added to alkali metal hydroxide solutions in the form of alkali metal compounds or the alkali metal compounds may be formed in situ by the addition of the acidic materials to solutions containing appropriate amounts of alkali metal hydroxide. Similarly the soaps may be formed in situ or added as such to alkali metal hydroxide solutions.

The specific examples given are only by way of illustration and are not intended to limit the invention to the specific quantities given or the particular compounds named. Mixtures of the various solventizers may be used as well as mixtures of different soaps. It is important, however, that sufficient quantities of free alkali, solventizer and soap be present to obtain the full benefits of the invention.

Although we have found that solutions containing from 5% of free caustic alkali up to the maximum amount soluble in the solution may be used, it is preferred to use solutions which contain not over 90% of the maximum amount soluble therein. Very effective results have been obtained with solutions containing from 8% to 25% of free sodium hydroxide or 10% to 40% free potassium hydroxide. The invention also contemplates the use of alcoholic alkali as well as aqueous alkali solutions.

Treating solutions in accordance with this invention can be regenerated in the same manner as caustic alkali solutions, namely, by boiling or by steam stripping, and reused either with or without adjusting the alkali concentration of the solution, and with or without further additions of naphthenic acids and/or phenols.

We claim:

1. In a method for removing acidic substances from liquid hydrocarbons, the step which comprises contacting said hydrocarbons with an aqueous solution containing at least 5% by weight of free caustic alkali, at least 10% by weight of soap of alkali-soluble alicyclic acid, calculated as acid, and a sufficient amount of phenolic compound, capable of acting as a solventizer, to dissolve the soap.

2. The step in accordance with claim 1 in which the soap comprises soap of naphthenic acid having in excess of 8 carbon atoms per molecule.

3. The step in accordance with claim 1 in which the caustic alkali is sodium hydroxide.

4. In a method for removing weakly acidic sulfur compounds from hydrocarbon oils, the step which comprises contacting said oils with aqueous alkali metal hydroxide solution containing at least 5% by weight of free alkali metal hydroxide, at least 10% by weight of soap of naphthenic acid calculated as acid, containing in excess of 8 carbon atoms per molecule and at least 5% by weight of a phenolic compound capable of acting as a solventizer.

5. The step in accordance with claim 4 in which the alkali metal hydroxide is sodium hydroxide and the amount of sodium hydroxide is between approximately 8% and 25% by weight.

6. The step in accordance with claim 4 in which the alkali metal hydroxide is potassium hydroxide and the amount of potassium hydroxide is between approximately 10% and 40% by weight.

7. The step in accordance with claim 4 in which the alkali metal hydroxide is sodium hydroxide, the amount of sodium hydroxide is between approximately 8% and 25% by weight and the naphthenic acid soap contains between about 11 and 16 carbon atoms per molecule.

8. The step in accordance with claim 4 in which the solution contains the following materials in approximately the indicated proportions by weight: 18% sodium hydroxide, 19% naphthenic acid and 6% cresol.

9. The step in accordance with claim 1 in which the phenolic compound is the product resulting from the reaction of an alkali metal hydroxide and cresol.

10. The step in accordance with claim 1 in which the phenolic compound is the product resulting from the reaction of an alkali metal hydroxide and a thiophenol.

11. The step in accordance with claim 1 in which the phenolic compound is the reaction product resulting from the reaction of an alkali metal hydroxide and a chlorphenol.

12. In a method for removing acidic sub-

stances from hydrocarbon fluids, the step which comprises contacting said fluids with a caustic alkali solution containing at least 5% by weight of free caustic alkali, an amount of alkali metal soap of naphthenic acid substantially in excess of that amount soluble in the caustic alkali solution in the absence of a solventizer and sufficient to materially enhance the ability of the caustic alkali solution to extract acidic substances from hydrocarbon fluids, and a sufficient amount of a phenolic compound capable of acting as a solventizer to dissolve the soap.

LAWRENCE M. HENDERSON.
GEORGE W. AYERS, JR.