Patented Sept. 9, 1947

2,427,083

UNITED STATES PATENT OFFICE

2,427,083

PROCESS OF REMOVING WEAKLY ACIDIC SUBSTANCES FROM OILS

Chester E. Adams, Highland, and Theodore B. Tom, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Application December 7, 1944, Serial No. 567,114

11 Claims. (Cl. 196—30)

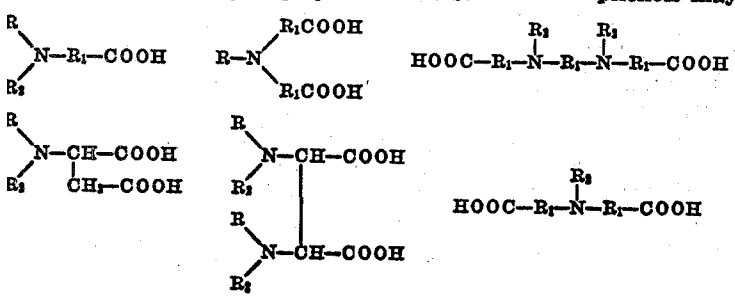
1

This invention relates to the extraction of weakly acidic substances from oils such as hydrocarbon oils and it relates more particularly to the refining of petroleum products, naphtha, gasoline, kerosene, and similar oils containing small amounts of weakly acidic substances such as mercaptans difficult to remove by ordinary alkali washing. Heretofore it has been proposed to facilitate the extraction of such weak acids as mercaptans, phenols, etc., by extraction with caustic alkali solutions containing mercaptan solubilizing agents called "solutizers." These solutizers are usually organic substances having a high solubility in the caustic solution, while changing the character of the caustic solution in some way not fully understood to increase the solubility of the weak acid in the caustic.

When employing solutizers, it is necessary to regenerate the caustic solution at frequent intervals to remove therefrom the weak acids, e. g. mercaptans, and recycle the regenerated caustic solution; otherwise the cost of the chemicals would be too great to be tolerated. Regeneration has been effected by distillation, by oxidation, or by other means.

It is an object of our invention to facilitate the extraction of mercaptans and other weak acids from oils by employing a more effective solutizer than those previously employed. Another object of our invention is to provide a solutizer for the extraction of mercaptans from naphthas, gasoline, etc. which is highly resistant to oxidation during regeneration. Other objects of the invention will be observed from the following description thereof:

According to our process, we employ as solutizers the N-substituted amino acids having either one or both —NH_2 hydrogens substituted with alkyl or other hydrocarbon radical. In general, the di-substituted amino acids are preferred for their increased resistance to oxidation. The following type formulas illustrate the class of compounds which we may employ as solutizers:



2

In the above formulas, R is alkyl, cycloalkyl, aryl or aryl-alkyl, R_1 is an alkylene group having from one to four carbon atoms, and R_2 is an alkyl radical or hydrogen. Typical substituted amino acids we may use are dimethyl-, diethyl- and dipropylaminoacetic acid, butylaminoacetic acid, dimethylaminobutyric acid and methylethylaminopropionic acid. In general we prefer to employ substituted amino acids having from 3 to 8 carbon atoms.

In the extraction of mercaptans from naphthas with a caustic soda or caustic potash solution having a concentration of about 5 to 25 per cent, we can employ about 5 to 35 per cent of substituted amino acid solutizer in the form of its sodium or potassium salt. Expressed in molarity, in most operations a free caustic concentration of about 2 to 5 is preferred, and such a solution will preferably contain about 1 to 4 molar concentration of solutizer. It is not necessary to employ pure substituted amino acids but mixtures of different substituted amino acids may be employed as well as mixtures of substituted amino acids with other substances having a solutizing action such as the phenols, the low molecular weight fatty acids, naphthenic acids, etc. The term "phenols" is used to denote the general class including the cresylic acids, chlorinated phenols, cresols, etc., the xylenols and others. In the extraction of naphthas, particularly cracked naphthas, it is commonly found that phenols are present in the naphtha in sufficient concentration to build up a considerable concentration in the caustic solution employed for extracting mercaptans therefrom. The concentration of phenols obtained in this way can be readily regulated, for example by pre-extraction of a part of the phenols with caustic solution, with liquid ammonia, or other suitable solvent for phenols. Excessive concentration of phenols collecting in the caustic solutizer solution may also be reduced from time to time by discarding a portion of the solution from which phenols may be sprung with acid if desired and

from which the solutizer may be recovered and returned to the system.

The unusual effectiveness of the substituted amino acid solutizers is indicated by the results obtained on extraction of a painter's naphtha solution containing butyl mercaptan. The data set forth in the table show the results obtained with dimethylamino acetic acid in comparison with amino acetic acid. The data also show the results obtained with mixtures of substituted amino acids with cresylic acid all in the form of their potassium or sodium salts employed in caustic potash or soda solutions as indicated. The procedure was as follows:

A naphtha solution of butyl mercaptan was prepared by adding sufficient butyl mercaptan to painter's naphtha to bring the copper number to 100. Five volumes of the resulting sour naphtha were stirred rapidly for ten minutes with one volume of the solutizer solution being tested. A nitrogen atmosphere was employed during the mixing operation to avoid oxidation of any mercaptan. The mixture was then allowed to settle for five minutes, the naphtha layer was separated, washed twice with water, and the copper number was then determined. The copper number is a true indication of the mercaptan concentration, the test being made in the following manner: A 100 ml. sample of naphtha is titrated with standard ammoniacal copper solution, 1 ml. of which is equivalent to 1 mg. mercaptan sulfur per 100 ml. (1 copper number). The end point is observed when the blue color fails to be discharged after shaking.

for example by stripping with steam, the alkali mercaptides being dissociated at elevated temperature, thus releasing the mercaptans from the caustic solution. We prefer, however, to effect regeneration by contacting the solution with air or oxygen at slightly elevated temperatures, for example 100 to 130° F. Under these conditions the mercaptans are oxidized to the corresponding disulfides which are insoluble in caustic and which may be removed as a separate layer. The separation of the disulfides can be facilitated by adding a suitable hydrocarbon solvent at this point in the system.

When employing the oxidation regeneration method, we may accelerate the oxidation by addition of various catalysts, preferably the polyphenols such as hydroquinone and catechol described in the patent of Ernest Pevere, U. S. 2,015,038 (September 17, 1935). We may also use pyrogallol, tannin, protocatechuic acid, gallic acid, and similar phenolic mercaptan oxidation catalysts. The amount of catalyst required for the purpose is usually of the order of 0.1 to 1 per cent.

Having thus described our invention what we claim is:

1. The process of removing weakly acidic substances from oils which comprises extracting said oils with an aqueous solution of caustic alkali and an alkali metal salt of an N-substituted amino acid in which the amino nitrogen is attached to at least one hydrocarbon radical.

2. The process of claim 1 wherein the concentration of caustic alkali is about 5 to 25 per cent and the concentration of substituted amino acid is about 5 to 35 per cent.

3. The process of removing weakly acidic substances from oils which comprises extracting said oils with an aqueous solution of a caustic alkali and an alkali metal salt of a dialkyl amino acid, having both alkyl groups substituted on the amino nitrogen.

4. In the process of extracting mercaptans from a petroleum distillate which comprises countercurrently contacting said distillate with an aqueous caustic alkali solution containing a solutizer in sufficient concentration to substantially increase the solubility of said mercaptans in said caustic solution, separating the caustic solution from the distillate, subjecting it to regeneration by removing dissolved mercaptans therefrom and recycling said caustic solution containing said solutizer to the contacting step for the extraction of further quantities of distillate, the improvement comprising employing as said solutizer an N-substituted amino acid in which the amino nitrogen is attached to at least one hydrocarbon radical.

Extraction of 100 copper number naptha

Composition of Caustic Solution	Copper No. of Naptha After Extraction	Partition Coefficient Kq.	Comments
6N KOH, 3N Dimethylaminoacetate	6	78	Emulsified.[1] Some salting out took place.
4N KOH, 2N Dimethylaminoacetate, N Cresylate	4	120	
3.6N KOH, 0.9N Dimethylaminoacetate, 1.8N Cresylate	<1	>495	About ½% entrainment.[2]
3N NaOH, 0.9N Dimethylaminoacetate, 1.7N Cresylate	7.5	62	About 2% entrainment settled out rapidly.
5.5N KOH, 2.7N Aminoacetate	27	14	Salted out at conc. 6-3.
4N KOH, 2N Aminoacetate, N Cresylate	10	45	
3.6N KOH, 0.9N Aminoacetate, 1.8N Cresylate	4	120	
3N NaOH, 0.9N Aminoacetate, 1.7N Cresylate	7.5	62	Emulsified badly.[3] 2% entrainment.

[1] Emulsion broken with small amount of Tretolite L-16503.
[2] The once-used solutizer solution was used again: copper No. 100 ⟶ 3.
[3] Emulsion broken with difficulty using Tretolite L-16503.

The efficiency of extraction is indicated by the coefficient, Kq which is the concentration of mercaptans in the caustic solution divided by the concentration remaining in the naptha.

It will be noted from the foregoing data that in practically all cases the extraction of mercaptans is more complete when employing the dimethylaminoacetic acid solutizer than when employing the unsubstituted amino acetic acid at the same concentration. Furthermore, the use of the unsubstituted amino acetic acid has a tendency to develop emulsions which are very troublesome, especially in large-scale commercial operations.

In carrying out our process of mercaptan extraction on a commercial scale, we prefer to extract the naptha countercurrently either in a series of mixers and settlers or in an extraction tower provided with suitable packing or baffles to insure efficient countercurrent contacting. The extracted naptha is discharged at the top of the tower while the caustic solution is withdrawn at the bottom and conducted to the regeneration step. The dissolved mercaptans may be discharged from the caustic solution by distillation,

5. The process of claim 4 wherein said regeneration is effected by oxidizing dissolved mercaptans in said caustic solution to disulfides by the action of oxygen and separating the resulting disulfides from the caustic solution.

6. In the process of sweetening sour petroleum distillates containing mercaptans which comprises extracting one such distillate with an aqueous caustic alkali solution having a concentration of about 2 to 5 normal free caustic and a solutizer serving the purpose of increasing the solubility of mercaptans in said caustic solution, separating said caustic solution from said distillate, regenerating said caustic solution by removing therefrom dissolved mercaptans and recycling the regenerated caustic solution to the extraction step for treatment of further quantities of distillate, the improvement comprising using as said solutizer an N-substituted amino acid in a concentration of about 1 to 4 molar, said N-substituted amino acid having at least one hydrocarbon radical attached to the amino nitrogen atom.

7. The process of claim 6 wherein said caustic solution is regenerated by contacting with air in the presence of a small amount of a polyphenol mercaptan oxidation catalyst, thereby converting said mercaptans to disulfides which are insoluble in said caustic solution and thereafter removing the said disulfides from the caustic solution before recycling to said contacting step.

8. The process of removing a weakly acidic substance from hydrocarbon oil which comprises extracting said oil with a strong aqueous caustic solution containing sufficient dimethylaminoacetic acid to increase substantially the solubility of said weakly acidic substance in said caustic solution.

9. The process of removing a weakly acidic substance from hydrocarbon oils which comprises extracting said oils with a strong aqueous caustic solution containing sufficient diethylaminoacetic acid to increase substantially the solubility of said weakly acidic substance in said caustic solution.

10. The process of removing a weakly acidic substance from hydrocarbon oils which comprises extracting said oils with a strong aqueous caustic solution containing sufficient dimethylaminobutyric acid to increase substantially the solubility of said weakly acidic substance in said caustic solution.

11. The process of removing mercaptans from petroleum distillates which comprises extracting said distillates with an aqueous solution of a caustic alkali containing a solutizer in sufficient concentration to increase substantially the solubility of said mercaptans in said solution, said solutizer consisting essentially of a mixture of alkali metal salts of cresylic acid and an N-substituted amino acid, in which the amino nitrogen is attached to at least one hydrocarbon radical.

CHESTER E. ADAMS.
THEODORE B. TOM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,228,041	Yabroff et al. (A)	Jan. 7, 1941
2,152,722	Yabroff et al. (B)	Apr. 4, 1939
2,364,582	Davis et al.	Dec. 5, 1944
2,341,878	Nixon et al.	Feb. 15, 1944
2,015,038	Pevere	Sept. 17, 1935
2,369,771	Bond (A)	Feb. 20, 1945
2,316,759	Bond (B)	Apr. 20, 1943
2,317,054	Henderson et al.	Apr. 20, 1943
2,164,851	Yabroff et al. (C)	July 4, 1939
2,156,577	Yabroff et al. (D)	May 2, 1939