

UNITED STATES PATENT OFFICE

2,425,777

PROCESS FOR THE EXTRACTION OF MERCAPTANS FROM HYDROCARBON OIL

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

No Drawing. Application August 22, 1945,
Serial No. 612,127

12 Claims. (Cl. 196—30)

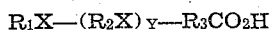
1

This invention relates to the extraction of weakly acidic substances from hydrocarbon solutions and more particularly it relates to the extraction of mercaptans from hydrocarbon oils such as petroleum distillates, naphtha, gasoline, kerosene, etc. In the manufacture of gasoline and other petroleum distillates known in refinery practice as "light oils," it has long been a problem to remove therefrom ill-smelling sulfur compounds which are primarily mercaptans. Certain processes such as the doctor treating process have been employed to convert mercaptans into other sulfur compounds such as disulfides which are less objectionable from the standpoint of odor. However, this conversion does not decrease the sulfur content of the gasoline and it has been found that the disulfides themselves are quite objectionable from the standpoint of gasoline detonation characteristics.

Numerous processes have been devised for extracting the mercaptans completely, thus producing a gasoline of higher knock rating and higher susceptibility to knock rating improvement resulting from the addition of tetraethyl lead. In general, these processes have employed strong alkali solutions in conjunction with certain mercaptan solubilizing agents known as solutizers.

One of the objects of this invention is to provide an improved solutizer for the extraction of weakly acidic substances from petroleum distillates. Another object of the invention is to provide a process of removing mercaptans more effectively from gasoline and other petroleum distillates by means of a solution which can be readily regenerated and recycled in the extraction operation. A further object of the invention is to provide a solutizer which is substantially nonvolatile and which will not be lost from the treating solution by dissociation and evaporation. A still further object of the invention is to provide a solutizer which is sufficiently effective in removing mercaptans from naphthas to produce a naphtha which will pass the doctor test without further treatment.

According to our invention, we employ for the treatment of hydrocarbon distillates alkaline solutions of solutizers having the following generic formula:



in which R_1 is an alkyl, substituted alkyl, or hydrogen radical, R_2 is an alkylene radical, R_3 is an alkylene or substituted alkylene radical, X is either oxygen or sulfur, preferably oxygen, and

2

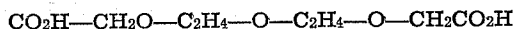
Y is a simple whole number. Examples are the ethers of glycol- and polyglycol substituted aliphatic acids, and their corresponding thio and thioxy derivatives. For convenience, these compounds are termed herein "polyether acids," their common characteristic being a chain of at least two ether or thioether linkages in combination with an organic acid radical. The simplest compound of the class is methoxymethoxy-acetic acid and its corresponding thio derivative, methio-methio-acetic acid; likewise methiomethoxy-acetic acid and methoxymethio-acetic acid may be employed. Ethioethoxy-acetic acid and ethoxyethoxy-acetic acid are both excellent solutizers. These solutizers generally contain from 4 to 10 carbon atoms.

Polyethoxy acids may be conveniently prepared from glycol and its derivatives. Thus, glycol monomethyl ether (methylcellosolve) is readily condensed with monochloroacetic acid by first treating with sodium methylate and driving off the methanol in a vacuum.

Besides the polyethers and thioethers of acetic acid, we may also employ similar derivatives of higher molecular weight acids, e. g. propionic and butyric acids, as well as the dibasic acids such as malonic and succinic. We may also employ the polysubstituted polyethers, the simplest of which are bismethoxy succinic acid and bismethoxy acetic acid. Likewise we may employ the dibasic acids wherein the polyether linkage joins the two acid radicals as in glycol diacetic acid



which may be prepared by condensation of the sodium derivative of glycol with sodium monochloroacetate followed by liberation of the acid from its salt. Also we can use such compounds as the following:



the generic formula of which is



where R is an alkylene radical and n is a whole number.

In carrying out our process, the hydrocarbon distillate containing mercaptans or other weakly acidic material is contacted preferably in a countercurrent extraction tower with a strong alkaline solution of the polyether acid solutizer. For this purpose, sodium or potassium hydroxide may be used, preferably the latter, in a concentration of about 2 to 6 normal free caustic above that combined with the solutizer agent. The

concentration of solutizer employed will usually be within the range of about 5 to 40 per cent on the basis of free polyether acid in the alkali solution. Usually the polyether concentration falls within the range of 1.5 to 4 molar. The extraction step is preferably carried out at ordinary temperature, for example 40 to 100° F., and the solutizer solution containing dissolved mercaptans or other weakly acidic substance is withdrawn from the extractor and separately regenerated after which it is recycled to the extraction step. The regeneration operation consists in removing from the caustic solutizer solution the dissolved mercaptans or other weakly acidic substances, and is preferably carried out by blowing with air, for example at a slightly elevated temperature, e. g. 120 to 130° F. It is desirable to avoid subjecting the solutizer solution to a temperature sufficiently high to accelerate materially hydrolysis of the carboxy ether employed.

In the regeneration operation, part of the mercaptans may be removed by dissociation and evaporation and part by the oxidizing action of the air converting them to disulfides which are no longer soluble in the solutizer solution. These disulfides may be removed as an upper oily layer and, if desired, a hydrocarbon or other immiscible solvent may be employed to assist in their removal from the regenerated solutizer solution. The solutizer solution is then recycled to the continuous extraction step of the process for the accumulation of more mercaptans.

The regeneration reaction may be accelerated by employing catalysts which have the ability to speed the oxidation of the mercaptans. For this

with an alkali washing step to remove part of the phenols, cresols, etc., thus preventing an excessive amount of such phenolic substances accumulating in the solutizer solution. In the treatment of such phenol-containing stocks, however, there is a distinct advantage to permitting a controlled amount of such phenols, cresols, etc., accumulating in the solutizer solution, and we have found that the combination of cresols and our polyether acids provides a very effective reagent for extracting mercaptans. We prefer to control the amount of cresols in the range of about 1 to 3 normal concentration. Inasmuch as the distillate extracted by such a solution has been found to carry away in solution a small amount of cresols in the concentration which is in equilibrium with that in the solutizer solution, and inasmuch as cresols exert a valuable antioxidant effect on the treated gasoline, particularly in the case of cracked stocks, it is clearly desirable to employ a solutizer solution containing cresols. Other solutizers besides cresols may be employed with our polyether acids and a suitable proportion of polyether acids is a molar ratio to the other solutizer of 0.2 to 4.

The following table gives the results obtained in the extraction of a sour naptha containing primarily butyl mercaptan as an example of a weakly acidic substance. Removal of the butyl mercaptan is indicated by the copper number of the naptha. Extraction was carried out in the ratio of one volume of solutizer solution to five volumes of naptha in a single batch extraction step. The particular solutizers employed are indicated in the table. The copper number of the naptha treated was 100 before extraction.

Test No.	Composition of Solutizer Solution	Cu No. of Naptha After Extraction	Butyl Mercaptan Distribution Coefficient, Kq	Comments
1-----	6N KOH, 3N C ₂ H ₅ OCH ₂ COOK	8	58	
2-----	4N KOH, 2N C ₂ H ₅ OCH ₂ COOK, N K cresylate	4	120	
3-----	6N KOH, 3N C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ COOK	0.5	995	Reuse: Cu No. 100 → 1.5.
4-----	4N KOH, 2N C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ COOK, N K cresylate	1	495	Reuse: Cu No. 100 → 2.5.
5-----	3N KOH, 2N C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ COOK, 1.5 N K cresylate	0.5	995	1% entrainment. Emulsion broken with Tretolite. Reuse: Cu No. 100 → 2.
6-----	6N NaOH, 2N C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ COONa	2.5	195	Reuse: Cu No. 100 → 4.
7-----	4N NaOH, 2N C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ COONa, N Na cresylate	2	245	Reuse: Cu No. 100 → 3.5.
8-----	6N KOH, 2N C ₂ H ₅ SCH ₂ CH ₂ OCH ₂ COOK	5.5	86	
9-----	4N KOH, 2N C ₂ H ₅ SCH ₂ CH ₂ OCH ₂ COOK, N K cresylate	1.0	495	
10-----	3N KOH, 2N C ₂ H ₅ SCH ₂ CH ₂ OCH ₂ COOK, 1.5 N K cresylate	<0.5	>995	

purpose certain alkali-soluble metal oxides may be employed, such as the oxides of lead, tin, etc. but we prefer to employ compounds of the character of phenols and polyphenols in accordance with the teaching of the U. S. patent of Pevere 2,015,038 (September 17, 1935). According to this method there is added to the solutizer solution a small amount of a phenol or polyphenol such as hydroquinone, catechol, pyrogallol, gallic acid, tannic acid, etc., using a concentration of about 0.1 to 1 per cent, thereby greatly increasing the rate of regeneration in the presence of air or oxygen. One very significant benefit resulting from the use of these phenolic catalysts is that they enable regeneration to be carried out at a lower temperature, for example room temperature, thereby avoiding the cost of heating and cooling large volumes of solution. Corrosion of equipment is also reduced.

In the treatment of certain petroleum stocks, particularly cracked gasoline containing small amounts of phenolic compounds, especially cresols, it is desirable to precede the extraction

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.

The copper number referred to above is determined by titrating a 100 ml. sample of naptha 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.

As a general rule when the concentration of mercaptans in a naptha stock falls below about one copper number it will exhibit a negative doctor reaction and therefore may be technically considered "sweet." It will be noted that several of the extractions described hereinabove effected a reduction of copper number below one illustrating the high efficiency of our new solutizers and their usefulness in producing acceptably sweet stocks on extraction in only a single stage. In general, however, multistage extraction is employed, for example, countercurrent tower ex-

5

traction, in which case acceptably sweet stocks are obtainable by the use of our new solutizer over a wide range of conditions either alone or in combination with other solutizers such as the phenols exemplified by cresylic acid. It sometimes may be more economical practice to remove the major portion of the mercaptans from the stock by solutizer extraction and then complete the sweetening in a further separate sweetening operation with lead plumbite doctor, hypochlorite, or other well-known sweetening method to produce a stock which will pass the doctor test where that is desired.

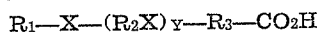
Having thus described our invention what we claim is:

1. The process of extracting weakly acidic substances from hydrocarbon distillates which comprises contacting said distillates with a solution of an alkali metal hydroxide and a solutizer comprising an alkali metal salt of a polyether acid.

2. The process of claim 1 wherein the polyether acid is ethoxy-ethoxy-acetic acid.

3. The process of claim 1 wherein the polyether acid is methoxymethoxy-acetic acid.

4. The process of extracting weakly acidic substances from hydrocarbon distillates which comprises contacting said distillates with a solution of an alkali metal hydroxide and a solutizer which is an alkali metal salt of an acid of the following general formula:



wherein R_1 is an organic radical of the class consisting of alkyl and substituted alkyl radicals, R_2 is an alkylene radical, R_3 is an alkylene radical, X is an element of group VI of the periodic system with atomic number of 8 to 16 and Y is a simple whole number.

5. The process of removing mercaptans from a sour petroleum distillate which comprises contacting said distillate with a solution of an alkali metal hydroxide and a solutizer comprising an alkali metal salt of a polyether acid.

6. The process of claim 5 wherein said alkali metal is potassium.

7. The process of removing mercaptans from sour hydrocarbon distillates which comprises extracting said distillates with a solution of an alkali metal hydroxide and a solutizer comprising a mixture of an alkali metal cresylate and an alkali metal salt of a polyether acid containing from 4 to 10 carbon atoms.

8. The process of claim 7 wherein the concentration of free alkali metal hydroxide in the said solution is about 2 to 6 normal, the concentration of alkali metal cresylate is about 0.5 to 3 normal, and the concentration of said polyether acid is about 1 to 3 normal.

9. The process of removing mercaptans from a sour hydrocarbon distillate which comprises ex-

6

tracting said distillate countercurrently with a solution of an alkali metal hydroxide containing about 3 to 6 normal free alkali and about 1 to 3 normal polyether acid in the form of its alkali metal salt.

10. The process of removing mercaptans from a sour hydrocarbon distillate which comprises extracting said distillate with a solution of an alkali metal hydroxide containing glycol diacetic acid in the form of its alkali metal salt in a concentration of at least 0.5 normal.

11. In the process of removing mercaptans from a sour petroleum distillate wherein said distillate is contacted with a solution of an alkali metal hydroxide in which the mercaptans are dissolved, the alkali solution is separated from the distillate and regenerated by the action of an oxygen-containing gas whereby the mercaptans are converted to disulfides insoluble in the said alkali solution, the said disulfides are separated from the alkali solution and the resulting solution is returned to the contacting step for removal of mercaptans from additional amounts of petroleum distillate, the improvement comprising increasing the solubility of mercaptans in said alkali solution by adding thereto a solutizer material comprising an alkali metal salt of a polyether acid.

12. In the process of removing mercaptans from a hydrocarbon distillate wherein said distillate is contacted with a solution of an alkali metal hydroxide containing a small amount, of the order of 1%, of a phenolic oxidation catalyst, the alkali solution containing mercaptans and said oxidation catalyst is separated from the hydrocarbon distillate, subjected to oxidation with air in a regeneration zone whereby said mercaptans are converted to disulfides insoluble in said alkali solution, and the regenerated alkali solution is recycled to the contacting operation for the removal of mercaptans from additional amounts of petroleum distillate, the improvement comprising employing as a mercaptan solutizer in said alkali solution an alkali metal salt of a polyether acid.

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
2,186,398	Yabroff (A) -----	Jan. 9, 1940
2,212,106	Yabroff (B) -----	Aug. 20, 1940
2,381,859	Ayers et al. -----	Aug. 14, 1945
2,369,771	Bond -----	Feb. 20, 1945
2,273,104	Steilman -----	Feb. 17, 1942
2,015,038	Pevere -----	Sept. 17, 1935