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REFINING OF MINERAL OILS

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6 Claims. (Cl. 196—32)

The present invention is concerned with the refining of mineral oils. The invention more particularly relates to an improved process for the removal of mercaptan compounds from oils, especially from petroleum oils boiling in the motor fuel and gas oil boiling ranges. In accordance with the present process, objectionable mercaptan compounds are removed from oils containing the same utilizing an alkaline solution such as an alkali metal hydroxide solution containing dissolved therein an oxygenated amino compound. The amino compound is characterized by comprising a six member ring structure having an oxygen atom and a nitrogen atom in the ring linkage. When utilizing a treating solution of this character, mercaptan compounds are efficiently removed in an economical manner. Furthermore, the solution may be readily regenerated for recycling to the treating zone.

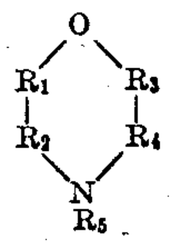
It is known in the art to refine oils such as petroleum oils by various procedures in order to produce products of a satisfactory quality. For example, it is known in the art to remove objectionable mercaptan compounds from petroleum oils utilizing a number of operations. One operation comprises treating the mercaptan-containing feed oil with a so-called "doctor solution" which comprises a sodium hydroxide solution of lead oxide under conditions to convert the mercaptan compounds to soluble alkyl disulfide compounds. This operation does not reduce the total sulfur content of the oil but merely converts the sulfur compounds into relatively innocuous materials. In an operation of this character, the doctor treated oil containing soluble lead mercaptides is usually treated with free sulfur so as to precipitate the lead as lead sulfide and to form the corresponding oil soluble relatively harmless alkyl disulfides.

One disadvantage of this process for the removal of mercaptans is that considerable care must be exercised with respect to the addition of the free sulfur. If insufficient sulfur be added, all the lead mercaptides are not removed from the oil which results in a product of inferior quality. On the other hand, if an excess of sulfur be added, this excess sulfur remains dissolved in the treated oil which increases its corrosiveness and in many instances necessitates rerunning of the oil. Thus, various suggestions have been made that these objectionable mercaptan compounds be removed from the oil in a manner to completely free or at least considerably lower, the total sulfur content of the treated oil. For example, it has been suggested that the oil be treated with an alkali metal hydroxide solution, such as with a sodium hydroxide solution. However, in order to remove the mercaptan compounds satisfactorily, particularly the relatively high boiling mercaptan compounds, it is necessary to use a relatively large quantity of the reagent based upon the volume of oil treated. This is particularly the case when treating relatively high boiling oils, as for example, those oils boiling in the heavy naphtha, heating oil, and gas oil boiling ranges, which oils boil in the general range from about 250° F. to about 750° F.

I have now discovered a process by which mercaptan compounds may be efficiently removed from petroleum oils containing the same. My process comprises utilizing a treating solution comprising a alkaline solution and a substance selected from the class of compounds which are characterized by being six member ring compounds and which are further characterized by having a nitrogen atom and an oxygen atom in the ring linkage.

The alkaline treating solution may be any suitable alkaline solution such as metallic carbonate solution, alkali metal or alkaline earth metal hydroxide solutions. It is, however, preferred that the alkaline solution comprise an alkali metal hydroxide solution as, for example, a sodium hydroxide solution or a potassium hydroxide solution.

The organic substance is selected from the class of compounds which are characterized by having the following structural formula:



in which R_1, R_2, R_3, and R_4 represent alkyl groups and in which R_5 represents hydrogen, an alkyl group, or an oxygenated alkyl group. Suitable organic substances are, for example, morpholine, $O(CH_2CH_2)_2NH$, 4 beta ethoxyethyl morpholine, $O(CH_2CH_2)_2N\ CH_2CH_2OC_2H_5$, and 4 morpholine ethanol, $O(CH_2CH_2)_2N\ CH_2CH_2OH$. I have found that particularly desirable results are secured when morpholine is employed in conjunction with a solution of sodium hydroxide.

The concentration of the respective constituents will vary widely depending upon the oil being treated, the particular alkaline solution being used, and the particular organic substance being employed. In general, it is preferred that the solution comprise from about 10% to 60% organic agent, preferably from about 40% to 50%, and that the remainder comprise an alkali metal hydroxide solution.

The quantity of treating solution employed per volume of oil being treated likewise will vary considerably depending upon the character and

concentration of the mercaptan compounds present as well as upon the particular treating reagent used. In general it is preferred to employ from about 10 to about 50 volumes of a morpholine-sodium hydroxide solution per 100 volumes of oil being treated. The operating conditions may also vary considerably. Temperatures in the general range from about 32° F. to about 140° F. may be employed. It is, however, preferred to employ temperatures in the range from about 40° F. to 80° F. The oil and treating reagent may be contacted by a batch, a semi-batch operation, or by a countercurrent treating operation. Usually a continuous countercurrent operation is preferred. The time of contact is also adjusted and regulated so as to secure the desired removal of the objectionable mercaptan compounds. The time of contact will be a function of the above enumerated factors.

The treated oil and the spent alkaline reagent are separated by suitable means, after which the alkaline solution may be regenerated and recycled to the treating zone. In general, it is preferred to regenerate the spent alkaline solution by treating the same with steam under conditions to form the mercaptans which are volatilized and removed overhead.

In order to illustrate the invention further, the following example is given which should not be construed as limiting the same in any manner whatsoever.

Example

Segregated portions of a cracked petroleum oil boiling in the motor fuel boiling range were treated in several operations. In one operation a potassium hydroxide was employed while in the other operations the treating solution comprised potassium hydroxide and morpholine. The results of these operations are as follows:

	Untreated cracked naphtha	Treated with potassium hydroxide	Treated with potassium hydroxide solution of [1] morpholine			Treated with water solution of [1] morpholine
Composition of reagents:						
KOH 140 gms./liter, per cent		100	60	60	60	
Morpholine, do			40	40	40	50
Operating conditions:						
Treating temp., °F		75	75	75	75	75
Treat, per cent		10	10	2X10	3X10	10
Gasoline inspections:						
Mg. mercaptan/100, ml	36	23	11	5	1.5	36
Mercaptan removal, per cent		36	69	86	96	None
Sulfur, per cent by weight	0.204	0.190	0.167	--	0.159	
Gravity, °A. P. I.	50.9					
Distillation, Engler—						
Initial boiling point, °F	172					
Per cent distilled at—						
212° F	4.5					
257° F	27.5					
302° F	54.5					
356° F	82.5					
392° F	95.0					
410° F	97.0					
Final boiling point, °F	421					
Recovery, per cent	98.5					
Loss, do	0.9					

[1] Tetrahydro-1, 4-oxazine or diethylenimide oxide.

Although any alkali solution may be used, I particularly prefer to employ alkali metal hydroxide solutions, especially a sodium hydroxide solution. When utilizing a sodium hydroxide solution, I prefer to use a solution of from about 2 to 10 normal sodium hydroxide solution calculated on the total solution, and to use from about 0.2 to 0.4 volume of sodium hydroxide solution per volume of oil.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the removal of mercaptan compounds from oil which comprises contacting a feed oil containing mercaptan compounds with a treating agent comprising an alkali metal hydroxide solution and morpholine.

2. Process as defined by claim 1 in which said alkali metal hydroxide solution comprises a sodium hydroxide solution.

3. Process as defined by claim 1 in which said alkali metal hydroxide solution comprises a sodium hydroxide solution and in which the feed oil is treated with from about 0.2 to about 0.4 volume of treating agent per volume of oil.

4. Process for the removal of mercaptan compounds from oil, which comprises contacting a feed oil containing mercaptan compounds with a treating agent comprising an alkali metal hydroxide solution containing about 10% to 60% of morpholine.

5. Process according to claim 4 in which the treating solution contains about 40% to 50% of morpholine.

6. Process according to claim 4 in which the alkali metal hydroxide solution is within the limits of about 2 to about 10 normal.

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