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PROCESS FOR REFINING HYDROCARBON OILS

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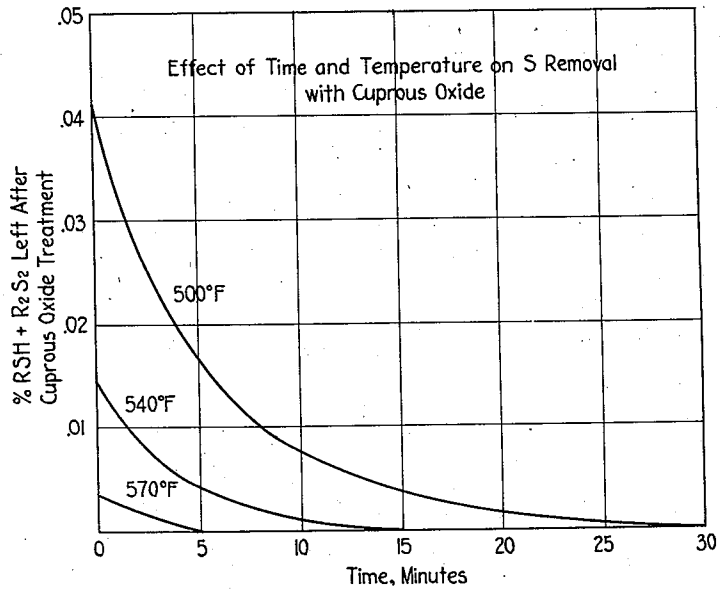

Fig. 1

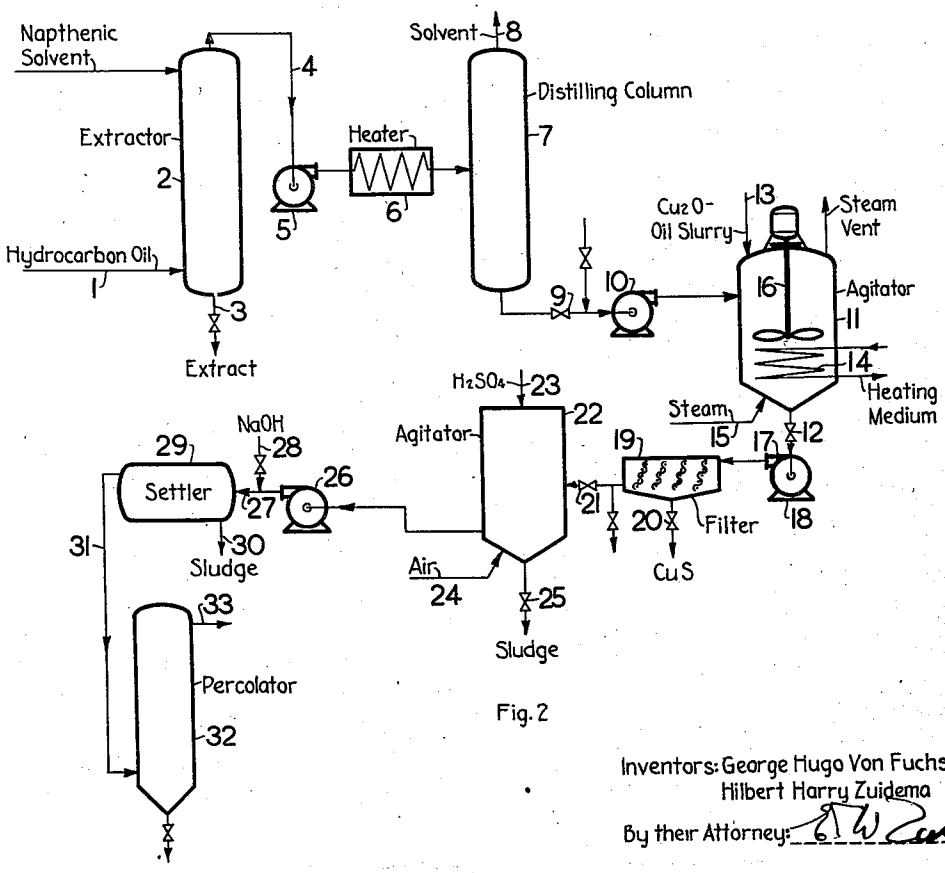

Fig. 2

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PROCESS FOR REFINING HYDROCARBON OILS

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10 Claims. (Cl. 196—30)

This invention relates to improvements in the treatment of hydrocarbon oil free from asphalts and more particularly to an improved process of sweetening and desulfurizing lubricating oils.

An object of the invention is to provide a process whereby hydrocarbon oils free from asphalts such as distillates, or residual oils deasphaltized by treatment with normally gaseous hydrocarbons, may be treated to sweeten and desulfurize the same, thereby producing oils which are suitable for use as burning oils or in transformers, electrical switches, refrigerators, etc. Our process is particularly applicable to lubricating distillates or bright stocks. Oils treated by our process have particularly good stability in the presence of metallic copper. Another object is to remove mercaptan sulfur without converting it to disulfide sulfur. Still another object is to reduce disulfide sulfur already contained in the oil to mercaptans and removing the mercaptans so formed.

Broadly, our process comprises treating the lubricating oils free from asphalt in the liquid state preferably at about 500 to 600° F. with cuprous oxide substantially free from cupric oxide to convert the mercaptans to cuprous sulfide which is insoluble in the lubricating oil, and then removing the cuprous sulfide from the oil in any suitable manner.

Our process is preferably applied to lubricating raffinates obtained by extraction with a suitable so-called naphthenic solvent i. e. which preferentially dissolves aromatic hydrocarbons from mixtures comprising paraffins and aromatics, and is followed advantageously by treatment with H_2SO_4.

Lubricating oils which have received no oxidation treatment normally contain varying amounts of mercaptans but usually are substantially free from disulfides. It is generally known that mercaptans are harmful and for this and other reasons oxidation treatments capable of converting mercaptans to disulfides are frequently employed. Such treatment may comprise the conventional H_2SO_4 and Doctor treatments, oxidation with air, etc. Now, however, we have found that disulfides as well as mercaptans are harmful in regard to sludge formation in electrical equipment. One of the tests which we have used for the determination of sludge forming tendencies in oils used in electrical equipment consists of heating a sample of an oil at 302° F. for 8 hours in the presence of copper. The oil is observed for color and sludge before and after the test. The following experimental data show the effect of disulfide sulfur in small quantities on the formation of sludge and darkening of the oil.

TABLE I

8 hour test at 302° F. in the presence of copper

Sample	Percent disulfide sulfur	N. P. A. color after test
1	.001	4½ (no sludge).
2	.001	1 (no sludge).
3	.015	5 (trace of sludge).
4	.050	4 (considerable sludge).
5	.060	6 (considerable sludge).

Disulfides form sludge in the presence of copper even at lower temperatures, e. g. 203° F. when the time of the treat is extended.

TABLE Ia

96 hour test at 203° F. in the presence of copper

Sample	Percent disulfide sulfur	Appearance after test
6	.001	No sludge.
7	.015	Trace of sludge.
8	.060	Sludge.

According to these data the maximum disulfide sulfur content that may be tolerated is of the order of .015% calculated as sulfur and preferably not more than .01%.

The above data indicate that a successful treatment for the production of sludge-resisting electrical oils must be capable of removing mercaptans without forming disulfides as well as removing disulfides originally present. Our treatment with cuprous oxide converts mercaptans to cuprous sulfide according to the reactions:

$$Cu_2O+2RSH \rightarrow Cu_2(SR)_2+H_2O \quad (1)$$

$$Cu_2(SR)_2+\text{heat} \rightarrow Cu_2S+RSH+R-CH=CH_2 \quad (2)$$

The mercaptans formed in Equation 2 react with more cuprous oxide so that all of the mercaptans are eventually converted to cuprous sulfide and olefins, provided that at least one mol of cuprous oxide is used in the treatment for every mol of mercaptans contained in the oil. Disulfides may also be removed with cuprous oxide provided that the temperature of the treatment is high enough to cause thermal decomposition of the disulfides into more reactive compounds such as mercaptans. For complete thermal decomposition of disulfides, temperatures as high as 600° F. may be required.

A complete removal of mercaptans or disulfides is not always necessary as it has been found that about 0.01% of mercaptan sulfur may be tolerated in the finished oil therefore slightly less than one mol of Cu_2O per mol of mercaptans actually or potentially present may be sufficient to reduce the sulfur content enough to produce a non-sludging oil. However, the amount of Cu_2O should be sufficient to reduce the harmful sulfur to a point not to exceed 0.01%. In general, we prefer to use between 1 and 2 mols of Cu_2O per mol of potential mercaptan sulfur. By harmful sulfur or mercaptan sulfur potentially present we mean the mercaptan sulfur actually present and that which may be liberated by decomposition of disulfides.

Since, as is shown in Table I and I*a*, disulfides are harmful, it is essential that conditions leading to the formation of them be avoided. Thus substances capable of converting mercaptans to disulfides under the conditions of the treatment should be absent.

For example, there should not be substantial amounts of air present or easily reducible metal oxides such as CuO, Fe_2O_3, Ni_2O_3, etc. A cuprous oxide therefore must be employed which contains as low as possible an amount of cupric oxide, cupric oxide being the most common impurity of commercial cuprous oxide, for cupric oxide reacts under the conditions of the treatment with mercaptans according to the reaction:

$$CuO+2RSH \rightarrow Cu(SR)_2+H_2O$$
$$2Cu(SR)_2 \rightarrow R_2S_2+Cu_2(SR)_2$$

yielding the objectionable disulfide.

The following data show the effects of cuprous oxides containing different amounts of cupric oxide.

TABLE II

Cuprous oxide color	Content of CuO	Harmful sulfur in oil after contact with 0.5% Cu_2O	
		RSH sulfur	R_2S_2 sulfur
	Percent	*Percent*	*Percent*
Bright red Cu_2O	3.49	.001	.001
Brown red Cu_2O	22.2	.024	.017

Since as previously pointed out, the maximum permissible disulfide sulfur content in the treated oil is below .015% the maximum permissible content of cupric oxide in the cuprous oxide is limited to that which yields disulfide sulfur below this limit. This maximum will vary with the amount of cuprous oxide used in the treatment. The more cuprous oxide required, the less the tolerance for cupric oxide. In general we prefer cuprous oxide which contains less than 10% and preferably less than 5% cupric oxide. We have found that such a cuprous oxide is normally satisfactory and generally has a bright red color as distinguished from brown or brown red cuprous oxide. As may be seen from the following analysis bright red cuprous oxides normally contain less than 5% cupric oxide whereas brown red contains about 10% or more.

	Appearance	CuO
		Per cent
1	Bright red	3.4
2	....do	3.5
3	....do	3.3
4	Brown red	9.8
5	....do	16.5

The cuprous oxide may be added to the lubricating distillate to be treated in the dry state or in the form of an oil slurry. Contact may be maintained for the necessary length of time by mechanical agitation or by passing a gas free from free or easily available oxygen through the mixture such as steam, nitrogen, hydrogen, etc. The operative temperature range is between 400° F. to 700° F., and as Cu_2O at high temperatures in the neighborhood of 700° F. may induce cracking, we prefer to limit the time in this temperature range so as to avoid substantial production of olefines. Olefines, as is well known, adversely affect the stability of hydrocarbon oils. At about 700° F. desulfurization is usually accomplished in a few seconds and it is therefore possible to operate in this temperature range of incipient cracking without danger of the formation of excessive amounts of olefines, however, because of this possibility of cracking, the maximum temperature should be substantially below 700° F. unless the contact time is very short. At temperatures below 400° F. mercaptan sulfur is converted too slowly and incompletely to be of practical value. Temperatures between 450° F. and 600° F. and preferably between 500° F. and 570° F. being particularly useful. The effect of time and temperature is illustrated in Figure I of the attached drawing which represents the actual removal of mercaptans by our process with time at various temperatures, the % of mercaptan sulfur and disulfide sulfur left after the treatment being plotted against time for several temperatures. The abscissae in Figure I represents the time required to remove the sulfur compounds after the temperatures in question were reached. As will be seen substantially complete removal of mercaptans can be achieved at 500° F. in about 30 minutes or in about 5 minutes at 570° F. without substantial formation of disulfides.

After completion of the above treatment, the cuprous sulfide formed in the process must be removed together with the excess of cuprous oxide. This may be done by settling, filtration or other conventional methods.

Since olefins are formed and soluble copper compounds and undesirable compounds may result from the reaction or may have been introduced from an outside source, the cuprous oxide treatment of the hydrocarbon oil should be followed by a conventional sulfuric acid treatment. Such a treatment comprises adding 10 to 50 lbs. of sulfuric acid of 90 to 100%, preferably 93 to 98% concentration, per barrel of hydrocarbon oil to be treated and agitating, if desired, with air. Acid components from the treatment may be removed by conventional means such as neutralization with aqueous caustic soda, alcoholic caustic soda, pressure hydrolysis, contact clay treatment, etc., and in addition the oil may be further refined by percolation through a naturally active clay such as Florida, Attapulgus and Ohmstead clays. Instead of removing olefins by acid treatment they may be removed or be converted to nonsludging compounds by other known means such as hydrogenation.

The treating stock which we use is preferably a raffinate obtained by extracting a mineral oil with a naphthenic solvent such as liquid SO_2, phenol, cresylic acid, furfural, beta beta di-chlor ethyl ether, nitrobenzene, etc., and such raffinate should be free from asphalt. Unextracted oils usually contain reactive compounds other than mercaptans which also react with cuprous

oxide and thus increase the amount of cuprous oxide required for removing mercaptans.

Referring now to Figure 2 of the attached drawing which represents a flow diagram of a preferred form of our process. A hydrocarbon oil free from asphalt is passed through line 1 into extractor 2, where the oil is separated into a raffinate and extract by extraction with a suitable naphthenic solvent. An extract layer is drawn off through line 3 and the raffinate is taken overhead through line 4, picked up by pump 5 and pumped through heater 6 into fractionating column 7 where the raffinate is freed of solvent by fractional distillation. The solvent passes through line 8 and the raffinate is conveyed through line 9 by pumps 10 and is discharged into agitator 11. An amount of cuprous oxide preferably in the form of an oil slurry is added by way of line 13 in an amount slightly in excess of the mol proportion necessary to convert the harmful sulfur contained in the lubricating oil to cuprous sulfide. The mixture in the agitator is heated to about 500° F. to 600° F., by passing a suitable heating medium through coil 14, and maintained at this temperature for about 5 to 30 minutes. The oil may be agitated by steam from line 15 and/or by mechanical agitator 16 during the heating to insure thorough contact with the Cu_2O. At the end of the necessary time the Cu_2O treated oil is withdrawn by pump 18 through valve 12 and line 17 and is forced through filter 19 to remove the cuprous sulfide and excess cuprous oxide. The cuprous sulfide and excess cuprous oxide are discharged through discharge line 20 and the filtrate passes through line 21 into agitator 22. In this agitator about 10 to 50 lbs. per barrel of concentrated H_2SO_4 are added to the hydrocarbon oil by way of line 23 and the mixture agitated by air from line 24. This treatment removes the unsaturates, and also soluble copper compounds and traces of solvent if present, in the form of a sludge which settles and may be removed through discharge 25. The treated oil is conveyed by pump 26 through line 27 into which NaOH is fed from line 28 in quantities sufficient to neutralize the oil. The neutralized oil now passes into separator 29 and sludge settles out and is removed by way of line 30. The refined oil is now ready for use, but if desired it may be further refined by passing it through line 31 and clay percolator 32 and thence through line 33 to storage.

The following example further illustrates our process.

A raffinate, obtained by extracting a West Texas distillate by the Duo Sol process, said raffinate having a viscosity at 100° F. of 61 Saybolt Universal seconds, NPA color of 1 and containing mercaptans was heated at 500° F. for one-half hour with .5% by weight of a bright red cuprous oxide using steam for agitation. The mercaptan sulfur was converted to cuprous sulfide which along with the excess cuprous oxide was filtered off. Analysis of the filtrate showed no measurable quantity of mercaptan or disulfide sulfur, showing that the reaction with the cuprous oxide was quantitative. This oil was acid treated with 50 lbs. per barrel of 98% H_2SO_4, neutralized with aqueous NaOH and was percolated through percolation clay. The resulting oil having the properties of a transformer oil was subjected to the before described test at 302° F. in the presence of copper. No sludge was formed.

We claim as our invention:

1. In the process of refining a hydrocarbon oil selected from the group consisting of lubricating and electrical oils free from asphalt containing harmful sulfur in the form of mercaptan sulfur, the steps comprising heating said oil in the liquid state at a temperature from about 400° F. to 700° F. with at least 1 mol cuprous oxide per mol of said mercaptans under non-oxidizing conditions to convert mercaptan sulfur to cuprous sulfide and substantially to prevent conversion of mercaptans to disulfides.

2. Process of claim 1 in which the hydrocarbon oil is a bright stock.

3. Process of claim 1 in which the hydrocarbon oil is raffinate obtained by extracting mineral oil with a naphthenic solvent.

4. In the process of refining a hydrocarbon oil selected from the group consisting of lubricating and electrical oils free from asphalt containing harmful sulfur in the form of mercaptan and disulfide sulfur, the steps comprising heating said oil in the liquid state at a temperature above 400° F. and below cracking temperature, and under non-oxidizing conditions with at least 1 mol of a bright red cuprous oxide per mol of said mercaptans under conditions to convert mercaptan sulfur to cuprous sulfide and removing the cuprous sulfide so formed.

5. In the process of refining a hydrocarbon oil, selected from the group consisting of lubricating and electrical oils, and free from asphalt and containing sulfur in the form of mercaptan sulfur, the steps comprising heating said oil in the liquid state from about 450° F. to 600° F. under non-oxidizing conditions in the presence of at least 1 mol of a cuprous oxide substantially free from readily reducible metallic oxides per mol of said mercaptans under conditions to convert mercaptan sulfur to cuprous sulfide and removing the cuprous sulfide so formed.

6. In the process of refining a hydrocarbon oil selected from the group consisting of lubricating and electrical oils free from asphalt and containing harmful sulfur in the form of mercaptan sulfur, the steps comprising heating said oil in the liquid state at a temperature from about 500° F. to 570° F. under non-oxidizing conditions in the presence of at least one mol per mol of said mercaptans of a cuprous oxide containing less than 10% cupric oxide for a time sufficient substantially completely to convert the sulfur of said mercaptans to cuprous sulfide and separating the cuprous sulfide so formed.

7. In the process of refining a raffinate selected from the group consisting of lubricating and electrical oils, obtained by extracting a mineral oil with a naphthenic solvent, said raffinate containing harmful sulfur in the form of mercaptan and disulfide sulfur and being free from asphalt, the steps comprising heating said raffinate in the liquid state at a temperature from about 400° F. to 700° F. under non-oxidizing conditions in the presence of at least 1 mol of a bright red cuprous oxide per mol of said mercaptans for a time sufficient to convert said mercaptans to cuprous sulfide and olefins, separating the cuprous sulfide and removing the olefines from the resulting oil.

8. In the process of refining a raffinate obtained by extracting a lubricating oil with a naphthenic solvent which raffinate is free from asphalt and contains harmful sulfur in the form of mercaptan sulfur, the steps comprising heating said raffinate in the liquid state at a temperature of 400° F. to 700° F. under non-oxidizing conditions in the presence of at least 1 mol per mol of said mercaptans of a cuprous oxide con-

taining not more than 10% cupric oxide for a time sufficient to substantially completely convert said mercaptans to cuprous sulfide and olefins separating the cuprous sulfide, subjecting the resulting oil free from Cu_2S to a treatment with concentrated sulfuric acid and neutralizing the acid treated oil.

9. In the process of producing an oil for electrical purposes which is non-sludging when subjected to an 8 hour test at 302° F. in the presence of copper, the steps comprising treating a raffinate produced by extracting a mineral oil with a naphthenic solvent, said raffinate having a viscosity suitable for an electrical oil, containing harmful sulfur in the form of mercaptan and disulfide sulfur, and being free from asphalt, by heating in the liquid state with at least 1 mol of a bright red cuprous oxide per mol of mercaptans in said raffinate at a temperature of 450° F. to 600° F. under non-oxidizing conditions for a time sufficient to convert substantially all of said mercaptans to cuprous sulfide and olefins, separating the cuprous sulfide so formed and unreacted cuprous oxide, subjecting the resulting oil to a treatment with 10 to 50 lbs. per barrel of sulfuric acid having a concentration of 95–98%, neutralizing the acid treated oil and percolating the neutralized oil through a bed of percolation clay.

10. In the process of refining a hydrocarbon oil selected from the group consisting of lubricating and electrical oils free from asphalt containing harmful sulfur in the form of disulfide sulfur, the steps comprising heating said oil in the liquid state to a temperature sufficiently high to convert disulfides to mercaptans and treating the heated oil at a temperature of about 400° F. to 700° F. with at least 1 mol of cuprous oxide per mol of said harmful sulfur under non-oxidizing conditions to convert mercaptans to cuprous sulfide and substantially to prevent conversion of mercaptans to disulfides.

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