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RECLAMATION OF USED LUBRICATING OILS BY SULFURIC ACID TREATMENT

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13 Claims. (Cl. 208—179)

ABSTRACT OF THE DISCLOSURE

Carbonaceous impurities and sludge are removed from mineral lubricating oils which contain acylated nitrogen-containing, polymeric ashless dispersants by contacting the oil with at least about 20 lbs., often about 25 to 40 lbs., per barrel of oil, of aqueous sulfuric acid having a concentration of about 80 to 90 volume percent, allowing the resultant mixture to settle and then separating a lubricating oil of improved viscosity and color.

This invention relates to an improved process for the removal of carbonaceous impurities and sludge from mineral lubricating oils having present therein acylated nitrogen-containing, polymeric ashless dispersants. More particularly this invention concerns the use of sulfuric acids for removing carbonaceous inpurities and sludge from petroleum lubricants containing amide, imide or amidine-type ashless dispersants.

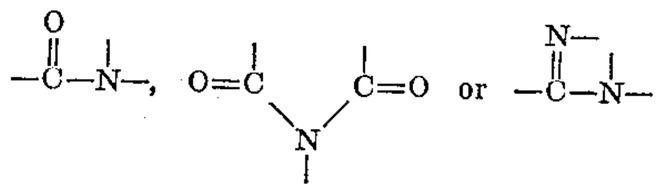
Removal of carbonaceous impurities and sludge from lubricating and industrial oils has generally been achieved by using high concentrations of sulfuric acids, that is concentrations of 98% and preferably even higher. In fact, fuming sulfuric acid has been considered even more desirable. Although sulfuric acids of these concentrations have been effective for removal of carbonaceous impurities and sludge from certain lubricants, they have been totally ineffective for this purpose in reclaiming lubricating oils provided with acylated nitrogen-containing ashless dispersants. The presence of such ashless dispersants in the lubricant appears to interfere with the settling of the acid sludge after the sulfuric acid treatment. Thus, highly concentrated sulfuric acid, for example, greater than about 98%, rather than refine the oil tends to hinder removal of the carbonaceous impurities and sludge. The net result is an increased amount of time required for settling and a poor recovery of oil possessing the desired color and viscosity. Thus, all attempts to purify lubricating oils provided with acylated nitrogen-containing ashless dispersants by chemical and physical means have met with little or no success.

It has now been found that mineral oils of lubricating viscosity containing acylated nitrogen-containing ashless dispersants, carbonaceous impurities and sludge when treated with an aqueous sulfuric acid solution having a sulfuric acid concentration of about 80 to 95% by volume, preferably about 85 to 95%, and allowed to settle, provide lubricating oils possessing excellent color and viscosity. The sulfuric acid solution can be added in a dosage of at least about 20 pounds per barrel of lubricating oil, preferably about 25 to 40 pounds per barrel. The lubricating oil can be treated with the sulfuric acid solution at room temperature up to about 500° F., preferably about 100 to 140° F. The contact time will vary but is a time sufficient to effect removal of carbonaceous impurities and sludge and provide upon settling a lubricating oil of improved viscosity and good color, for instance an ASTM color of less than 5, preferably less than 2. Ordinarily, the contact time is at least about 0.5 hour up to about 5 hours. The settling time after the acid treatment can vary anywhere from about

18 to greater than about 40 hours, preferably about 18 to 22 hours.

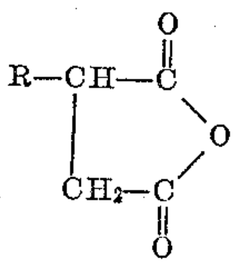
The used lubricating oils treated by the process of the present invention can be any mineral oil of lubricating viscosity, for instance, a solvent-extracted or solvent-refined oil obtained in accordance with conventional methods of solvent refining lubricating oils. Generally, lubricating oils have viscosities from about 20 to 250 SUS at 210° F. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crude, and if desired, a blend of solvent-treated Mid-Continent neutral and Mid-Continent bright stocks may be employed.

The ashless dispersants present in the lubricating oils to be treated by the process of the present invention, known as acylated nitrogen-containing, polymeric dispersants, their use and manner of preparation are well known in the lubricating oil art. By acylated nitrogen is meant a nitrogen atom which is directly attached to a carboxylic acid or anhydride radical so as to form an amide, imide or amidine linkage, i.e.

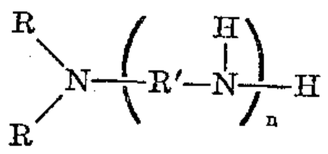


The carboxyl carbon atom is, in turn, attached either directly or indirectly to a substantially aliphatic polymer of sufficient molecular weight to render the dispersant mineral oil-soluble. Examples of these compounds, their method of preparation, and use are found throughout the patent literature, for instance, in U.S. Patent Nos. 2,800,-452; 3,018,250; 3,018,291; 3,024,195; 3,024,237; 3,048,-544; and 3,087,936.

Among the oil-soluble, acylated nitrogen-containing, polymeric dispersants often preferred for use in mineral lubricating oils are the amidic and imidic reaction products of (A) a monohydrocarbylsuccinic anhydride corresponding to the general formula:



wherein R is a hydrocarbon radical, preferably aliphatic, having a molecular weight of about 400 to 4000, preferably about 750 to 2000, and (B) a polyamine corresponding to the general formula:



wherein R is selected from the group consisting of hydrogen and hydrocarbon radicals of 1 to about 30 carbon atoms, R′ is a divalent alkylene radical of 2 to about 14 carbon atoms, and *n* is 1 to about 10.

The hydrocarbyl substituent on the succinic anhydride group can advantageously be supplied by a polymerized olefin, preferably an alpha-olefin and preferably of 2 to about 30 carbon atoms. Thus, an olefin such as, for instance, ethylene, propylene, 1-butene, 2-butene, isobutene or their higher homologues or mixtures thereof can be polymerized to a molecular weight of about 400 to 4000. In addition to the polymerized olefin, there may also be present in the substantially aliphatic hydrocarbyl radical copolymerized ethylenically unsaturated aromatic monomers such as styrene and its homologues, e.g., vinyl toluene, alpha methyl styrene, etc., and/or diolefins such as butadiene and isoprene. The polymer can then be reacted in the absence of coplymerization catalysts with maleic anhydride in approximately equimolar quantities

to form an addition product of maleic anhydride and the polyolefin, i.e., to form a monohydrocarbylsuccinic anhydride.

Suitable polyamines for reaction with the monohydrocarbylsuccinic anhydride include monoalkylene diamines, dialkylaminoalkylamines and the polyalkylene-polyamines. Illustrative of suitable monoalkylene diamines are ethylene diamine, propylene butylene diamine, octylene diamine, etc. Examples of suitable dialkylaminoalkylamines are dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, diethylaminopropylamine, diethylaminoamylamine, dipropylaminopropylamine, methylpropylaminoamylamine, propylbutylaminoethylamine, etc. Non-limiting examples of the polyalkylenepolyamine reactants are diethylenetriamine; triethylenetetramine; tetraethylenepentamine; polyethyleneimine; di-(methylethylene)triamine; hexapropyleneheptamine; tri(ethylethylene) tetramine; penta - (1 - methylpropylene - hexamine, tetrabutylenepentamines; etc.

The acylated nitrogen-containing ashless dispersants are often present in lubricating oils in amounts of about 0.5% to 3% by weight and may even be as high as about 6 to 10% by weight.

EXAMPLE

A railroad diesel engine lubricating oil containing an acylated nitrogen-containing ashless dispersant and contaminated with carbonaceous impurities and sludge had the following composition:

Base oil (89.3 volume percent):
- 56% 600 SUS at 180° F. Mid-Continent Neutral Oil;
- 16% 1200 SUS at 100° F. Naphthenic Base Oil;
- 28% 2000 SUS at 100° F. Naphthenic Base Oil.

Additives (10.7 volume percent):
- 3.6% Basic calcium mahogany sulfonate [1];
- 4.9% Calcium salt of condensation product of octylphenol, formaldehyde and diethylene triamine;
- 2.2% acylated nitrogen-containing ashless dispersant[2];
- 0.001% Dow Corning fluid (a defoaming agent).

[1] A 45% concentrate in mineral oil solution which analyzes: 3% calcium; base No. 28.0.
[2] An approximately 48% concentrate in mineral oil of the reaction product prepared by reacting polyisobutylene having a molecular weight of approximately 1000 with maleic anhydride and then reacting the resulting polyisobutenyl succinic anhydride with tetraethylene-penta-amine.

The above-identified contaminated lubricant was contacted with an aqueous solution of sulfuric acid in varying concentrations for about 1 hour at about 120° F., and

the resulting viscosity, color and amount of acylated nitrogen-containing ashless dispersant remaining after treatment was recorded in the table below.

TABLE

	1	2	3	4	5	6	7	8	9
Acid Strength, percent	104.5	98	95	95	90	85	80	80	66
Dosage, lbs./Bbl.	30	30	30	15	30	30	36	30	30
Settling Time, Hr.	40	40	40	40+	20	18	21	22	22.5
Oil Losses, Wt., Percent:									
Sludge	(1)	(1)	36	(2)	10.5	9.5	9.4	8.9	(3)
Filtering	(1)	(1)	4	(2)	11.4	8.3	9.8	9.9	(3)
Overhead	(1)	(1)	14	(2)	13.1	13.7	13.5	13.7	(3)
Final Yield, Wt., Percent			46	--------	65	69	67	68	--------
Reclaimed Oil Inspect.: [4]									
API Gravity			26.1	--------	25.8	25.4	25.3	25.3	--------
KV/100° F., cs.			211.3	--------	191.2	206.7	217.8	218.7	--------
KV/210° F., cs.			15.32	--------	14.04	14.68	15.10	15.10	--------
ASTM Color			L2.0	--------	L2.0	L5.0	Dark	Dark	--------
Acylated nitrogen-containing ashless dispersant			None	--------	None	0.14	0.71	0.54	--------

[1] Layer separation poor.
[2] No layer separation.
[3] Acid oil would not filter.
[4] Clay treated with 15 lbs. Clay/Bbl. of oil at 550° F. for 30 minutes.

As can be seen from the data listed above, acid treatment with a sulfuric acid concentration less than 98% was very effective. For example, a 90% sulfuric acid concentration treatment of the railroad diesel engine lubricant containing 2.2% of the acylated nitrogen-containing ashless dispersant resulted in high recovery of oil possessing excellent color and viscosity. However, for acid concentrations of 98% or greater, layer separation was very poor. The data also demonstrate the importance of using a sufficient dosage in the treatment.

It is claimed:

1. A method for removing carbonaceous impurities and sludge from a mineral oil of lubricating viscosity containing the same and an acylated nitrogen-containing, polymeric ashless dispersant, which comprises contacting said mineral oil with at least about 20 lbs. per barrel of mineral oil of aqueous sulfuric acid having a concentration of about 80 to 90% by volume, settling the contacted mixture and separating a mineral oil of lubricating viscosity, improved viscosity and good color.

2. The method of claim **1** wherein the ashless dispersant is present in the mineral oil in an amount of about 0.5 to 10% by weight.

3. The method of claim **1** wherein the lubricating oil has a viscosity in the range of about 20 to 250 SUS at 210° F.

4. The method of claim **1** wherein the sulfuric acid has a concentration of about 85 to 90%.

5. A method for removing carbonaceous impurities and sludge from a mineral oil of lubricating viscosity containing the same and an acylated nitrogen-containing, polymeric ashless dispersant, which comprises contacting said mineral oil with about 25 to 40 lbs. per barrel of mineral oil of aqueous sulfuric acid having a concentration of about 85 to 90% by volume, settling the contacted mixture and separating a mineral oil of lubricating viscosity, improved viscosity and good color.

6. The method of claim **1** wherein the sulfuric acid has a concentration of about 80%.

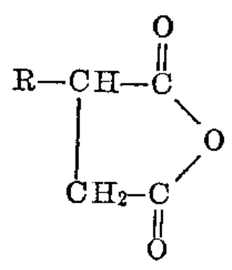
7. The method of claim **1** wherein the sulfuric acid has a concentration of about 85%.

8. The method of claim **1** wherein the sulfuric acid has a concentration of about 90%.

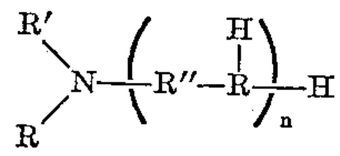
9. A method for removing carbonaceous impurities and sludge from a mineral oil containing same, said mineral oil having a viscosity in the range of about 20 to 250 SUS at 210° F. and additionally containing about 0.5 to 10% by weight of an acylated nitrogen-containing, poly-

meric ashless dispersant, which comprises contacting said mineral oil at about 100 to 140° F. with about 25 to 40 lbs. per barrel of mineral oil of aqueous sulfuric acid having a concentration of about 80 to 90% by volume, settling the contacted mixture and separating a mineral oil of improved viscosity and color.

10. The method of claim **9** wherein the ashless dispersant is a reaction product of (A) a monohydrocarbylsuccinic anhydride corresponding to the general formula:



wherein R is a hydrocarbon radical of about 400 to 4000 molecular weight, and (B) a polyamine corresponding to the general formula:



wherein R′ is selected from the group consisting of hydrogen and hydrocarbon radicals of 1 to about 30 carbon atoms, R″ is a divalent alkylene radical of 2 to about 14 carbon atoms, and *n* is 1 to about 10.

11. The method of claim **10** wherein the sulfuric acid has a concentration of about 80%.

12. The method of claim **11** wherein the sulfuric acid has a concentration of about 85%.

13. The method of claim **12** wherein the sulfuric acid has a concentration of about 90%.

References Cited

Nelson: "Petroleum Refinery Engineering," third ed., 1949, pub. McGraw-Hill Book Co., Inc., N.Y., 1949, pp. 252 to 257.

HERBERT LEVINE, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

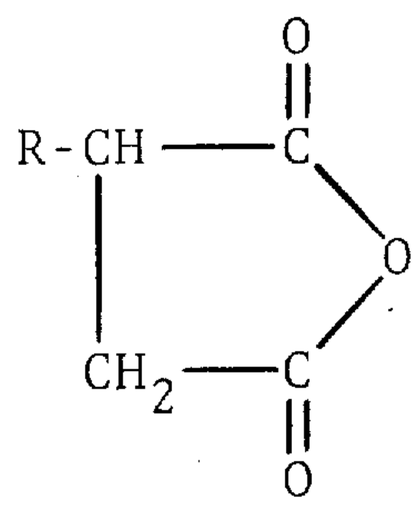
Patent No. 3,376,216 April 2, 1968

Donald D. Carlos et al.

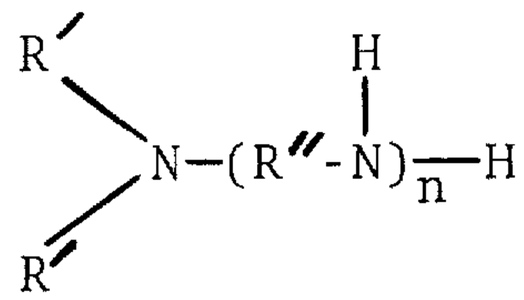
It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 43, "(1-methylpropylene" should read -- (1-methylpropylene) --. Column 5, line 7, beginning with "10. The method" cancel all to and including "1 to about 10." in line 10, column 6, and insert the following:

10. The method of claim 9 wherein the ashless dispersant is a reaction product of (A) a monohydrocarbylsuccinic anhydride corresponding to the general formula:



wherein R is a hydrocarbon radical of about 400 to 4000 molecular weight, and (B) a polyamine corresponding to the general formula:



wherein R′ is selected from the group consisting of hydrogen and hydrocarbon radicals of 1 to about 30 carbon atoms, R″ is a divalent alkylene radical of 2 to about 14 carbon atoms, and n is 1 to about 10.

Signed and sealed this 13th day of January 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents