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METHOD OF TREATING MINERAL LUBRICATING OILS

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5 Claims. (Cl. 196—13)

This invention relates to a method of treating mineral lubricating oils and it pertains more particularly to the art of preparing lubricating oils stable to oxidation and sludging.

Petroleum is essentially a mixture of hydrocarbons comprising several groups or homologous series of compounds, such as the paraffins, hydroaromatics, aromatics, polymethylenes, and various other series of compounds in which the hydrogen to carbon ratio is even lower than in the above classes. A large number of individual compounds of each series are present and have different boiling points, physical and chemical properties. In the various types of crude petroleum commonly known as paraffin base, naphthene or asphalt base, and mixed base oils, these various series of hydrocarbons are present in different proportions. For example, in paraffin base oils such as those from the Appalachian field, there is a relatively high proportion of paraffinic hydrocarbons having a chain structure and a high hydrogen to carbon ratio, whereas in the Gulf Coastal oils there is a high proportion of naphthenic hydrocarbons and hydrocarbons with ring structures and low hydrogen to carbon ratio. The mixed base oils, such as those from Oklahoma and the Mid-Continent area, are in general intermediate between these two extreme types.

In normal refining of crude petroleum, the fractions of varying distillation ranges which are successively obtained by distillation of the oils partake of the general character of the crude; for example, lubricating oils derived from Appalachian crudes will show paraffinic characteristics, whereas the lubricating oils derived from Gulf Coastal oils show naphthenic characteristics. The distillates from the mixed base crudes, such as those from the Mid-Continent area, will show characteristics common to both the naphthenic and paraffinic oils. An important property of paraffinic lubricating oils is their low viscosity temperature coefficient or rate of change of viscosity with temperature. This property makes them particularly suitable for certain lubrication problems where high temperatures are encountered. At low temperatures also, these oils retain their fluidity better, an important consideration in cold weather operation of automobiles, for example. For this reason it is very desirable to separate the mixed base oil into their paraffinic constituents and non-paraffinic constituents.

The paraffinic characteristics of an oil may be expressed by its viscosity index. The expression "viscosity index", as used herein, refers specifically to the index defined by Dean & Davis in Chemical and Metallurgical Engineering, vol. 36, 1929, page 618. The viscosity index of a lubricating oil is an indication of its composition or type, i. e., whether it is a paraffin base or naphthene

base oil. Paraffin base oils are arbitrarily assigned a viscosity index of 100, naphthene base oils are assigned a viscosity index of 0, and mixed base oils lie between these extremes. For example, if an oil shows a viscosity index of about 85 to 90, it is evident that the oil is predominately paraffinic in nature.

One of the common ways of increasing the paraffinic content of a lubricating oil is to treat the oil with fuming sulfuric acid. The oil and acid are mixed and agitated in the proportion of about one to two pounds of fuming acid for each gallon of oil. The mixture is then allowed to settle and the acid layer, comprising sulfuric acid and acid sludge settles to the bottom and is drawn off. The top layer comprises an oil which is high in paraffinic compounds. Also, lubricating oil refined in this way contains a relatively large quantity of sulfonic compounds which must be removed before the oil can be satisfactorily used for most lubricating purposes, and this operation is often expensive and wasteful because of troublesome emulsions which are encountered. The quality of the acid treated lubricating oil can be fairly judged from two of its properties, that is, the viscosity index and stability against sludge formation. The sludge stability is determined by bubbling air at the rate of 10 litres per hour into a 250 cc. sample of oil at 340° F. Samples of 10 grams each are withdrawn at intervals and tested to determine the amount of sludge formed for each 10 grams of oil. When the amount of sludge has increased to 10 mg. the number of hours of oxidation is noted and the sludge stability of the oil is then expressed in hours for 10 mg. of sludge. The amount of sludge is determined by diluting the 10 gram sample of oil with hexane and then filtering off the hexane insoluble residue.

The following table shows the sludge stability of a Mid-Continent lubricating oil distillate of 21.3 A. P. I. gravity, 101.9 Saybolt viscosity at 210° F., and a viscosity index of 54, when treated with different quantities of fuming sulfuric acid.

Table I

Example	Amt. of fuming acid in pounds	Percent yield	Stability in hours 10 mg.	Viscosity index
1	1.5	47	66	81
2	2.7	35	125	92

From the above table it will be observed that a 2.7 pound acid treat increased the viscosity index of the oil from 54 to 92, and the treated oil had a sludge stability of 125 hours. Also, it will be noted that the yield is only 35%. From the above data it is apparent that a large quantity of oil is

lost when highly stable oils are prepared by acid treating.

Mixed base oils can be made more paraffinic, as indicated by the viscosity index, by extracting the naphthenic and naphthenic-like compounds, or sludge forming hydrocarbons, from the oil with organic solvents. The solvent extraction may be performed with single solvents or with mixed solvents, and the extraction may be performed in one or several stages. Oils prepared by solvent extraction have very high viscosity indices, but the oils produced in this way are not stable against sludge formation. We have found that a light sulfuric acid treatment following the step of solvent extraction will make the oils very resistant to oxidation. We have found that the oils prepared by organic solvent extraction are particularly unstable as to sludge formation, but a light acid treatment is also capable of making these oils very resistant to sludge formation.

We will describe our preferred process by extracting a Mid-Continent lubricating oil distillate with a single organic solvent, di(2 chlorethyl) ether, and then follow this extraction with a light sulfuric acid treatment. We will use the same oil as described in connection with Table I, that is, a Mid-Continent lubricating oil distillate of 21.3 A. P. I. gravity, 101.9 seconds Saybolt viscosity at 210° F., and a viscosity index of 54. It should be understood that our process is applicable to any mixed base lubricating oil. The lubricating oil and di(2 chlorethyl) ether are mixed in the ratio of 3 volumes of solvent for each volume of oil, and the mixture is then agitated and heated to the miscibility temperature. Generally the solvent or solvents are miscible with the oil within the range of 95–210° F. In this particular example we used a miscibility temperature of 155° F. After the oil and solvent have been heated to the miscibility temperature, the mixture is cooled to a temperature below the miscibility temperature where the solvent and extract separate from the highly paraffinic oil. The temperature at which this separation is effected is called the "extraction temperature." In this particular example we used an extraction temperature of about 65° F. It should be understood that the extraction temperature may vary with different oils and solvents, but generally the extraction temperature is at least 40° F. below the miscibility temperature. The uppermost layer of oil comprises the highly paraffinic oil, and this layer is referred to as the "raffinate."

The solvent and extract are withdrawn from the bottom of the agitator, and then the raffinate is stripped with an inert gas. Generally, the stripping is performed at a somewhat elevated temperature.

The raffinate is then given a light sulfuric acid treatment. In this example, we used one-half pound of 93% sulfuric acid for each gallon of raffinate. The oil and acid were mixed and agitated at about 100° F. for a short time, the acid layer was allowed to settle and was then drawn off. The acid treating may be performed at any suitable temperature, but generally a temperature within the range of 20 to 200° F. is satisfactory. Also, the quantity of acid may be varied in accordance with the quality of the oil desired, but generally from one-fourth to one pound of 80–98% sulfuric acid will give a very stable oil. It should be understood that the more highly concentrated acid may be used in smaller quantities.

Typical results illustrating the cooperation between solvent extraction and acid treating are given in the following table.

Example 1 shows the viscosity index, sludge stability and yield of the oil after solvent extraction, and Example 2 shows the viscosity index, sludge stability and yield of the oil after solvent extraction followed with a light acid treatment.

Table II

Example	Three volumes of di(2 chlorethyl) ether for each gallon of oil				
	Pounds of sulfuric acid per gallon of ext. oil	Acidity	Yield	Stability in hours 10 mg.	Viscosity index
1.....	0			66	93
2.....	0.5	93%	55%	125	94

It will be observed from Example 1 in the above table that solvent extraction, per se, produced an oil of high viscosity index. Before extracting, the oil had a viscosity index of 54, but by solvent extraction this was raised to a viscosity index of 93. Notwithstanding the high viscosity index, the sludge stability of the oil is relatively low. By comparing the oil prepared by solvent extraction, as set forth in Example 1 of Table II, with the oil prepared by acid treatment, as set forth in Example 1 of Table I, it will be observed that both oils have the same sludge stability, but the oil prepared by solvent extraction has a much higher viscosity index, that is, the solvent extracted oil is more paraffinic than the acid treated oil. It will be observed from Example 2 of Table II, that a one-half pound 93% acid treatment applied to the oil in Example 1 of Table II raises the sludge stability from 66 hours to 125 hours for 10 mg. of sludge. Also, the yield of oil is 55%, whereas with acid treating per se, see Example 2, Table I, the yield is 35% for a 125 hour oil. So, by using a light acid treatment after solvent extraction we can obtain a 55% yield of 125 hour oil having a viscosity index of 94, whereas by acid treating alone, as shown in Example 2 of Table I, a 35% yield of 125 hour oil having a viscosity index of 92 was obtained. Also, the combination of solvent extraction and 93% acid treating gave an oil with properties that could not be obtained with 93% acid treating alone.

A lubricating oil distillate of 22.8 A. P. I. gravity and 101 sec. Saybolt viscosity at 210° F. was given three successive di(2 chlorethyl) ether extractions and the raffinate was then given a light acid treatment. The volume of chlorinated ether used for each extraction was 66% of the volume of oil. The following table shows the results from this treatment.

Table III

	Yield vol.	Viscosity 210° F.	Viscosity index	Stability in hrs. 10 mg.
Three-stage extraction with di(2 chlorethyl) ether.	60%	80.5	86.5	60
Treatment with 1/4 of 93% H ₂ SO ₄ after the three-stage extraction....	55%	78.6	88	231

It will be observed that the light acid treatment raised the sludge stability of the solvent extracted

oil from about 60 hours to 231 hours. Also, the yield of finished product was 55% whereas if fuming acid treatment alone had been used to produce a 231 hour oil, the yield would have been much below 35%.

It is difficult to explain why such a small amount of acid treatment following solvent extraction of an oil should be so effective in raising the sludge stability of the oil, and at the same time give a high yield of finished product. Possibly the solvents remove the naphthenic compounds that usually protect the sludge-forming compounds, thereby making the sludge-forming compounds of the oil more vulnerable to the action of acids.

As pointed out above in connection with acid treated oils, a large quantity of soluble sulfonic compounds remained dissolved in the acid treated oil, and it is necessary to remove these sulfonic compounds before the oil can be used for most lubricating purposes. Several processes have been used to remove the sulfonic compounds, the most common of which is to treat the oil with a soap solution. By using our process of solvent extraction followed with a light acid treatment, we overcome the difficulty of having sulfonic compounds dissolved in the raffinate. The solvents remove, among other substances, those compounds which react with sulfuric acid and form sulfonic acids; consequently, when the oil is given a light acid treatment, the soluble sulfonic compounds are not formed to any appreciable extent and their removal constitutes no problem nor entails serious loss of oil.

As pointed out in the above process of chlorinated ether extraction, it is necessary to strip the raffinate of the solvent dissolved therein, but it is very difficult to remove the last trace of solvent from the oil. If all of the halogenated compound is not removed, it will eventually decompose and produce chlorine compounds which are very corrosive. Also, if the oil is extracted with other organic compounds they will dissolve in the raffinate and it is frequently very difficult or even impossible to remove the last trace. Frequently, the color of the oil is impaired when the oil is subjected to severe stripping. Also, if every trace of solvent is not removed from the oil, the oil frequently becomes discolored and deteriorated in other ways. This is particularly true of solvents such as furfural. We have found that by giving the oil a light acid treatment subsequent to the steps of solvent extraction and light stripping, the last traces of solvent that remain in the oil can be very satisfactorily removed and we thereby prevent corrosive and color forming compounds from remaining in the finished oil.

The raffinate, or highly paraffinic oil, which is to be given a light acid treatment, may be obtained by extracting oil with any suitable selective solvent or mixture of solvents which will remove the constituents responsible for low viscosity index. Examples of some of the single solvents suitable for extracting oils are halogenated ethers, nitroaryl compounds, aryl amines, phenols, halogenated esters, and heterocyclic compounds. The following table gives examples of some of the above compounds which may be used for extraction.

Table IV

73	Methyl 2-chlorethyl ether
	di(2-chlorethyl) ether
	Methyl chloropropyl ether
	Methyl 2-3 dichloropropyl ether
	Ethyl 2-3 dichloropropyl ether
75	Ethyl chloropropyl ether

Table IV—Continued

	2-chlorethyl propyl ether
	Dichlorisopropyl ether
	Dichloropropyl ether
	Nitrobenzene
	Nitrotoluene
	Nitroxylene
	Aniline
	Phenol
	Cresols
	Cresylic acid
	Ethyl chloracetate
	Ethyl dichloracetate
	Ethyl chlorpropionate
	2-chlorethyl acetate
	Methyl chloracetate
	2-chlorethyl propionate
	Furfural
	Dioxane
	Pyridine
	Nitronaphthalene
	alpha dichlorohydrins
	chlorohydrins

Mixed solvents are also very effective for extracting mixed base lubricating oils, particularly the low boiling ketones, esters or ethers may be mixed with any of the solvents selected from the above Table IV. The following table gives examples of some of the mixed solvents that may be used for solvent extraction.

Table V

	Acetone and nitrobenzene
	Acetone and di(2-chlorethyl) ether
	Acetone and furfural
	Acetone and dioxane
	Acetone and paraldehyde
	Acetone and dichlorobenzene
	Acetone and ethylene dichloride
	Acetone and phenol
	Acetone and aniline
	Acetone and pyridine
	Acetone and cresol
	Diacetone alcohol and nitrobenzene
	Diacetone alcohol and di(2-chlorethyl) ether
	Methyl ethyl ketone and di(2-chlorethyl) ether
	Methyl ethyl ketone and pyridine
	Methyl ethyl ketone and di(2-chlorethyl) ether
	Methyl ethyl ketone and phenol
	Methyl propyl ketone and nitrobenzene
	Methyl propyl ketone and di(2-chlorethyl) ether
	Methyl isopropyl ketone and furfural
	Ethyl acetate and nitrobenzene
	Ethyl acetate and di(2-chlorethyl) ether
	Ethyl acetate and furfural
	Ethyl acetate and nitrotoluene
	Ethyl acetate and paraldehyde
	Ethyl acetate and phenol
	Glycerine and phenol
	Glycerine and furfural
	Glycerine and aniline
	Glycol and aniline
	Glycol and phenol
	Glycol and furfural
	Propyl ether and nitrobenzene
	Isopropylether and nitrobenzene
	Isopropylether and chlorinated ethers
	Ethyl acetate and dioxane
	Ethyl acetate and ethylenedichloride
	Methyl acetate and nitrobenzene
	Methyl acetate and di(2-chlorethyl) ether
	Methyl acetate and phenol
	Propyl acetate and nitrobenzene
	Propyl acetate and di(2-chlorethyl) ether

Table V—Continued

	Propyl acetate and phenol
	Propyl acetate and furfural
	Propyl acetate and dichlorobenzene
5	Butyl acetate and phenol
	Butyl acetate and furfural
	Butyl acetate and paraldehyde
	Butyl acetate and di(2-chlorethyl) ether
	Butyl acetate and nitrobenzene
10	Ethyl propionate and nitrobenzene
	Ethyl propionate and di(2-chlorethyl) ether
	Ethyl propionate and phenol
	Methyl propionate and nitrobenzene
15	When any of the solvents set forth in Table IV or V are used to extract mixed base mineral oils, the ratio of solvent to oil is preferably from one to 5 volumes of solvent for each volume of oil. The mixed solvents usually comprise from one to four volumes of ketone, alcohol, ester or ether for each volume of the other solvent. For example, one volume of acetone and about two volumes of nitrobenzene are mixed and used to extract one volume of oil. The process, temperatures used, etc., as set forth in connection with the process of using di(2-chlorethyl) ether as a solvent, may in general be successfully used with the solvents given in Tables IV and V.

When a mixed base lubricating oil distillate is extracted with any of the above solvents, the raffinate is highly paraffinic, as shown by its viscosity index, but the oil is not as resistant to sludging as would be expected from its high viscosity index. For example a mixed base lubricating oil distillate of 21.6 A. P. I. gravity, 114 seconds Saybolt viscosity and a viscosity index of 56.5 was extracted with different mixed solvents, and the following table shows the effect of such extraction upon the viscosity index yield and sludge stability of the oil. One volume of oil was extracted with the mixed solvents set forth in the examples of the following table.

Table VI

Example	Components	Percent yield	Tot. vol. of components	Ratio of components	Viscosity index
1	Acetone and nitrobenzene	70	1.5	0.5:1	87.5
2	do.	66	3	1:2	93.0
3	Acetone and di(2-chlorethyl) ether	75.6	2	1:1	87.5
4	Acetone and dioxane	76	2	1:1	82.5
5	Acetone and paraldehyde	69.8	3	2:1	84
6	Acetone and dichlorobenzene	75	2	1.8:0.2	81
7	Acetone and ethylene dichloride	64.6	3	2:1	84.5
8	Acetone and phenol	79.6	1.5	0.5:1	82
9	Ethyl acetate and nitrobenzene	70	1.5	0.5:1	88
10	Diacetone alcohol and nitrobenzene	66	1.5	0.5:1	83.5

It will be observed from the above table, Example 2, that we can raise a 56.5 viscosity index oil to a 93 viscosity index oil, by extracting one volume of the oil with three volumes of solvent, said solvent comprising one volume of acetone and two volumes of nitrobenzene. It will also be observed that the other mixed solvents have varying degrees of effectiveness upon the viscosity index, but all of the mixed solvents raise the viscosity index from 56.5 to a viscosity index of 81 or above. Notwithstanding the high viscosity index, or paraffinicity of these oils, they are susceptible to sludge formation when used under

oxidizing conditions. Most of the oils prepared by the above extraction will produce 10 mg. of sludge in about sixty hours. Also the yield of oil after the acid treatment will be of the order of 5 to 10% below the yield given in the above table with the solvents alone, but if acid treating alone were used to produce oils with 81 to 93 viscosity index and sludge stability of 95 to 150 hours, the yield of finished oil would be very low, and of the order of 35 to 45%. It is apparent from the above data that a light acid treatment following an organic solvent extraction gives a higher yield of finished product than could be obtained by acid treating alone. Also, the oils prepared by solvent extraction and combined light acid treating have a good color, and clay treating may be eliminated.

The term "naphthenic hydrocarbons" is employed in the specification and claims in a generic sense to include the compounds that have a low viscosity index and rapid sludge forming characteristics, examples of which are the aromatic, aromatic-like, olefines, polymethylenes, nitrogen and sulfur compounds.

The method used for mixed solvent extraction followed with a light acid treatment may be the same as set forth hereinabove with single solvents. Also the oil may be extracted with a single solvent, then extracted with a mixed solvent, and then given a light acid treatment to raise the oxidation stability if desired. Also, if desired, the oils may be given a light acid treatment before the step of solvent extraction.

The theory set forth herein to explain the unexpected results obtained by sulfuric acid treating combined with solvent extraction of lubricating oils is not to be considered as limitations upon the scope of our invention, and though the present invention has been described in connection with the details of specific examples, neither is it intended that such examples shall be regarded as limitations upon the scope of the herein described invention except as set forth in the claims.

We claim:

1. The process for preparing a lubricating oil which is highly resistant to sludge formation from a mineral oil containing naphthenic and paraffinic hydrocarbons, which comprises extracting the oil with a solvent containing a halogenated ether and thereby separating the highly naphthenic compounds from the paraffinic compounds, then treating the highly paraffinic fraction with a small quantity of strong sulfuric acid.

2. The process for preparing a lubricating oil which is highly resistant to sludge formation from a mineral oil containing naphthenic and paraffinic hydrocarbons, which comprises extracting the oil with a solvent containing a halogenated ether and a ketone and thereby separating the naphthenic hydrocarbons from the paraffinic hydrocarbons, and then treating the paraffinic hydrocarbons with a small quantity of strong sulfuric acid.

3. The process for preparing a lubricating oil which is highly resistant to sludge formation from a mineral oil containing naphthenic and paraffinic hydrocarbons, which comprises extracting the oil with a mixture of acetone and di(2-chlorethyl) ether and thereby removing the naphthenic hydrocarbons from the paraffinic hydrocarbons, and then treating the highly paraffinic hydrocarbons with a small quantity of sulfuric acid.

4. The process for preparing a lubricating oil which is highly resistant to sludge formation from

5 a mineral oil containing sludge forming and paraffinic hydrocarbons, which comprises heating and agitating the oil with a solvent containing acetone and a chlorinated aliphatic ether, cooling the mixture until the oil separates into a highly paraffinic fraction of hydrocarbons and a fraction of sludge forming hydrocarbons, and then treating the highly paraffinic fraction with 80-98% sulfuric acid in the proportion of about one to one-half pounds of acid per gallon of oil.

10 5. The process for preparing a lubricating oil which is highly resistant to sludge formation from

a mineral oil containing sludge-forming and paraffinic hydrocarbons, which comprises heating and agitating the oil with an organic solvent containing acetone and nitrobenzene, cooling the mixture until the oil separates into a highly paraffinic fraction of hydrocarbons and a fraction of sludge-forming hydrocarbons, and then treating the highly paraffinic fraction of oil with 80-98% sulfuric acid in the proportion of about one to one-half pounds of acid per gallon of oil.

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