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PROCESS FOR REFINING MINERAL OILS

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This invention relates to the refining of mineral lubricating oils, particularly highly paraffinic oils which it is difficult to refine by the known sulfuric acid treatments.

It is generally accepted in the art that paraffinic hydrocarbons or cyclo-paraffins which have paraffinic side chains and are highly paraffinic in nature are the most valuable constituents of lubricating oils, and the various processes developed in late years to improve lubricating stocks, using selective solvents, such as sulfuric dioxide, nitrobenzene, BB' dichloroethyl ether, fufural, phenol, quinoline, and various solvent mixtures, such as benzol-sulfur dioxide, or employing pairs of solvents which are flowed countercurrently to each other, such as propane-cresylic acid, have all had for their main purpose the separation of undesirable unsaturated naphthenic and/or aromatic hydrocarbons from the desirable paraffinic hydrocarbons. Thus, a lubricating oil stock of low viscosity index may be extracted with one of the above selective solvents or solvent mixtures or solvent pairs in such a way that the paraffinic portion or raffinate which is to be finished to produce lubricating oils may have a higher viscosity index. Paraffinic lubricating oils with high viscosity indexes may also be obtained by simple distillation of certain Pennsylvania crudes.

The viscosity index of a lubricating oil is a measure of its paraffinicity, and is defined by a viscosity temperature relationship as described in "Viscosity variations of oils with temperature" by E. W. Dean and G. H. B. Davis, published in Chemical and Metallurgical Engineering, 1929, vol. 36, No. 10, page 618. Pennsylvania oils may have viscosity indexes of approximately 100, while naphthenic oils may have zero and even negative viscosity indexes.

Sulfuric acid has been commonly used in the treatment of lubricating oils to improve their color and stability by removing or polymerizing or rendering innocuous part of the unstable compounds present in the oil. It is possible to improve the viscosity index and increase the paraffinicity of hydrocarbon oil by solvent extraction methods; but it is difficult and often impossible to remove certain of these unstable compounds by these methods, and it has, therefore, been proposed to treat mineral oils first with a selective solvent to improve the viscosity index, and then with sulfuric acid, to improve the stability of the oil, the latter treatment being often accompanied by a slight increase in the viscosity index.

Oils of a highly paraffinic character, such as those obtained from certain Pennsylvania crudes,

or by extraction of lubricating fractions of less paraffinic crudes with a selective solvent in such a way that the paraffinic portion or raffinate has a viscosity index higher than about 70 or 80, however, do not readily lend themselves to further improvement by means of a treatment with sulfuric acid because of practical difficulties. When such highly paraffinic oils are treated with sulfuric acid a part of the reaction products remains so finely dispersed in the oil that none of the known means of coagulation can be successfully used to precipitate this, so called, "pepper" sludge. Moreover, some of the reaction products are soluble in the oil and are not removed therefrom by neutralization with the chemicals usually employed for this purpose. The use of clay alone, even in amounts larger than can economically be employed, yields unstable and often dark colored and even black oils. Dilute aqueous solvents and solvent mixtures, such as aqueous alcoholic caustic soda solution or aqueous solutions of acetone and alcohol, when used on these highly paraffinic and/or highly viscous oils containing the acidic reaction products, form stable emulsions. For example, aqueous solutions of alcohol or acetone containing more than 40% water are generally unsuitable for freeing such oils from acidic reaction products.

The present practice in regard to such paraffinic oils is to treat them with clay alone in sufficient quantities to obtain the desired color, stability, etc. As far as I have ascertained, no generally satisfactory method of acid treating such paraffinic oils with sulfuric acid is known.

The above difficulties are most pronounced in the treatment of the more viscous oils, and especially of residual oils, to the treatment of which my process is particularly adapted.

I have discovered a process by which it is possible to acid treat such refractive lubricating oils and to improve them to such an extent that bright stocks more stable than Pennsylvania or aluminum chloride refined bright stocks can be manufactured from crudes otherwise yielding bright stocks inferior to similar Pennsylvania stocks. Furthermore, the clay consumption is greatly reduced by the use of my process, with the result that bright stocks of higher quality can be obtained at lower cost from inferior crudes.

I have found that such paraffinic lubricating oils can be effectively treated in the following manner: The paraffinic oil is first treated with a concentrated sulfuric acid, such as between 80 and 100% H_2SO_4 , depending upon the viscosity

of the oil, and generally above 90% the more viscous oils requiring a more concentrated acid. Moreover, it may often be desirable to employ fuming sulfuric acid, as, for example, 20% oleum, particularly in the refining of highly viscous white oils. Air agitation may, if desired, be used during this treatment. The treated oil is settled or centrifuged to separate a sludge or acid phase, and obtain an oil phase which contains a pepper sludge in suspension. The resulting sour oil may, if desired, be treated with alkali and water, such as caustic soda solution, although I have found that best results are generally obtained without this step. This oil which may or may not have been neutralized, is then washed or extracted with an oxygenated water-soluble aliphatic compound having not more than six carbon atoms in the molecule. Acetone is my preferred solvent, but I may use other aliphatic ketones, such as ethyl-methyl ketone, diethyl ketone, as well as aliphatic alcohols and similar oxy-aliphatic compounds. I have found that the best results are obtained and emulsions are avoided when the ketone or alcohol contains not substantially more water than is necessary to render the solvent to be sufficiently immiscible with the oil to be readily separated therefrom. Substantially anhydrous acetone and/or alcohol may often be employed, but when such materials are too soluble in the oil the use of small amounts of water is necessary. If water is present, it should preferably, not exceed 10% of the ketonic or alcoholic solution and should in any case be less than about 40%. This washing step effectively removes the undesirable colored and unstable compounds formed in the course of the acid treatment, and the small amounts of sodium salts of the acid compounds present, or soaps, formed in the caustic soda treatment when used. After the separation of the acidic compounds with an anhydrous or substantially anhydrous solution of the oxygenated aliphatic compound, water may be added to wash out the residual oxygenated aliphatic compound which remains in solution without danger of forming emulsions, or the oil may be washed with a more dilute aqueous solution of the same or of a similar substance. If desired, the residual compound may be separated by vacuum or steam distillation. The washed oil is then finished by a treatment with clay, such as fuller's earth.

Different methods of contacting the acid and the oil have been developed to obtain economies or operating advantages. The most common methods comprise the steps of directly mixing the oil stock and the acid under optimum conditions in batch agitators or in continuous mixers, and separating the sludge and acid in the same or different vessels or by centrifuging. Any of these methods may be employed in my process, as will be apparent to those skilled in the art. If desired, the stock may be first diluted with naphtha, or gasoline, or any other similar light distillate. The quantity of acid to be used in my process will vary with the nature of the oil stock treated and the quality of the product desired. In general, I have found that from about ten to fifty lbs. of 66° Bé. (93%) acid per barrel (42 U. S. gal.) of oil to be satisfactory, although it is to be understood that my invention is not limited to the use of these quantities of acid, because smaller or larger amounts may often be employed. The temperature of the acid and the oil may be varied within wide limits, and

I have found that best results are obtained when operating between 10° C. and 60° C.

While I prefer to separate the acid and sludge from the sour oil before washing the latter with acetone, it should be noted that this is not absolutely necessary, and that, particularly when small amounts of acid are employed, it is possible to wash the acid treated oil with acetone or alcohol in the presence of the excess of acid.

The ketone or alcohol wash or extraction may be carried out immediately after the acid treatment, or after the sour oil has been aged for several hours to complete the reaction and "condition" the pepper sludge. The extraction may be carried out in any suitable manner, as by multiple- or single-batch extractions in an agitating and settling or centrifuging apparatus, or by countercurrent treatment in a series of mixing and separating devices, or in a packed contact tower. The quantity of the extracting agent employed depends, inter alia, upon the nature of the oil, the quantity of acid employed, and upon the nature of the extraction treatment, a smaller quantity of extracting agent being sufficient when a countercurrent method is employed. In general, I have found that extractions using from 100% to 800% of extracting agent to be satisfactory, although my invention is not limited to these quantities.

Any suitable clay, and particularly activated clay, of the type heretofore employed for clay treating lubricating oils may be employed in the finishing treatment. The quantity to be employed may be varied according to the nature of the oil, and I have found that quantities between 3% and 25% are suitable, although the more viscous and residual stocks require larger amounts, generally more than 5%.

According to another embodiment of my invention I may combine the acid treatment with the washing operation by contacting one volume of the oil with about one to eight volumes of a solution containing one part by weight of concentrated sulfuric acid to about five to twenty parts by weight of a lower aliphatic oxygenated compound having not more than six carbon atoms in the molecule, such as acetone, methyl alcohol, acetic acid, etc. The water content of the solution should be low enough to permit the acid to effect the desired reaction upon the undesirable components of the oil, and should preferably not be over one part by weight of water to nine parts of sulfuric acid. In treating very viscous oils even smaller quantities of water are desirable, and I generally prefer to have the acid stronger than about 96%. When there is a possibility of polymerizing or otherwise chemically affecting the oxygenated aliphatic substance by the presence of the strong sulfuric acid, the time of reaction should be short enough, and the temperature and water content controlled to prevent this. Certain of the above mentioned solvents, e. g., acetone, when used in the anhydrous or very concentrated state are extremely soluble in oil, and are difficult to separate. In these situations I may add water to the solution after the oil has remained in contact with the concentrated acid solution for a time sufficient to complete the desired reaction and removal of the sludge. The addition of water has the effect of rendering the acetone or similar solvent immiscible in the oil, and permitting a good separation of the oil from the solvent, acid, and reaction products. The lower aliphatic substances, and particularly the acetone, are effective

to prevent the formation of troublesome emulsions. The quantity of water added in this step may vary within wide limits; while I have obtained satisfactory results by diluting the acetone to produce a 60% aqueous acetone solution, I generally prefer to use smaller amounts of water, stronger aqueous solutions of acetone being readily separable from the oil. If a less soluble solvent, such as acetic acid is employed, a much smaller quantity of water or no water is added to effect the final separation.

This form of treatment may also be carried out according to a continuous method, by flowing a solution of sulfuric acid and a solvent counter-currently to the oil, through a liquid contact tower, or a series of mixers and settlers, etc., as is common in the extraction of oils with selective solvents.

Although the process of my invention can be successfully applied to long residuum raffinates (i. e. paraffinic portions of lubricating fractions obtained by the use of any of the known selective solvent extraction methods) or Pennsylvania long residuums containing the whole range of lubricating oils, neutrals, and residual oils, it is more specifically advantageous for the treatment of heavy residual oil or raffinates. Lubricating distillate raffinates, which can usually be treated by means of the conventional methods, may, however, also be treated in accordance with my invention.

The improved results which are obtainable from the application of my process are illustrated from the following examples:

Example I

A residual oil from Hendricks crude was extracted with propane and cresylic acid to yield a raffinate having the properties shown in the first column of the table. One portion of this raffinate was contacted with 20% activated clay and yielded an oil having the properties shown in column 2 of the table. Another portion was diluted with 25% of naphtha and acid treated at 70° F. with 25 lbs. of 68 Bé. sulfuric acid per barrel of oil. The treated oil was unsuccessfully subjected to centrifuging, practically no sludge being separated in this step. The centrifuged oil was then washed five times with 100% by volume of commercial acetone (i. e. with a total of 500% acetone) freed from the acetone, and contacted with 10% clay. The properties of the resulting oil are shown in column 3 of the Table I.

Table I

Sample No.	1	2	3
Treatment	Extracted with propane-cresylic acid	No. 1 finished with 20% activated clay	No. 1 acid and acetone treated as described above and finished with 10% activated clay
Gravity °A. P. I.	24.5	25.5	25.2
Say. univ. visc. at 210° F.	140	130	105
Viscosity index.	74	78	94
Color N. P. A.		4½+	4+
Stability towards oxidation:			
Say. univ. visc. at 210° F. after 0 hrs.		130	105
48 hrs.		150	115
96 hrs.		216	141
144 hrs.		455	230

The above data show the marked improvement

of the viscosity index, as well as of the stability towards oxidation when using my improved process. The oxidation stability test was performed according to the Indiana oxidation method, as outlined in National Petroleum News, 1933, vol. 25, No. 37, page 27.

Example II

A heavy Mid-Continent residual oil was extracted with furfural to produce a raffinate having the properties shown in the table. One portion was finished with 20% of activated clay, and another portion was diluted with 40% of naphtha and acid treated at 70° F. with 25 lbs. of 66 Bé. sulfuric acid per barrel of oil. Air was blown through the mixture of oil, naphtha and acid until traces of "pepper" sludge were formed, and the resulting product was centrifuged. The resulting sour oil was extracted five times with 100% commercial acetone, freed from the acetone, and finished with 20% activated clay. The results are shown in Table II.

Table II

Sample No.	1	2	3
Treatment	Extraction with furfural	No. 1 finished with 20% activated clay	No. 1 acid and acetone treated as described above and finished with 20% activated clay
Gravity °A. P. I.	24.4	25.1	25.4
Say. univ. visc. at 210° F.	172	159	156
Viscosity index.	88	89	95
Conradson carbon.	3.41	1.3	0.70
Color N. P. A.		8+	5+
Stability towards oxidation:			
Say. univ. visc. at 210° F. after 0 hrs.		159	156
48 hrs.		190	185
91 hrs.		269	252
144 hrs.		296	298
192 hrs.		Too heavy	403

Example III

A Pennsylvania bright stock was acid treated as described in Example II, extracted with 300% by volume of acetone, and finished with 3% by weight of clay, with the results shown in Table III:

Table III

Sample No.	1	2
Treatment	Pennsylvania bright stock	No. 1 acid and acetone treated as described above and finished with 3% clay
Gravity °A. P. I.	26.7	27.6
Say. univ. visc. at 210° F.	142	129
Viscosity index.	98	104
Color N. P. A.	D7+	4½+
Stability towards oxidation:		
Say. univ. visc. at 210° F. after 0 hrs.	142	129
48 hrs.	180	145
96 hrs.	235	185
144 hrs.	515	235
192 hrs.	Too heavy	305
240 hrs.		410

These examples further indicate the marked improvement in the viscosity index and color, as well as in the stability which is effected by my method of treatment, and indicate the diversity

of oils which may be treated in accordance with the present invention.

I claim as my invention:

1. In the process of refining a highly paraffinic lubricating oil by treating same with sulfuric acid under conditions to form a pepper sludge which is incapable of settling, the step of extracting the oil containing pepper sludge with a substantially oil-insoluble solvent containing at least 60% of a water-soluble aliphatic oxy-hydrocarbon of not more than six carbon atoms under conditions to dissolve the pepper sludge substantially without dissolving the oil and to form two layers: a treated oil layer substantially free from sludge and solvent, and a substantially oil-free solvent layer containing the sludge, and separating the layers.
2. In the process of refining a highly paraffinic lubricating oil by treating same with sulfuric acid under conditions to form a pepper sludge which is incapable of settling, the step of extracting the oil containing pepper sludge with a substantially oil-insoluble solvent containing at least 60% of a water-soluble aliphatic oxy-hydrocarbon of not more than six carbon atoms selected from the group consisting of alcohols and ketones under conditions to dissolve the pepper sludge substantially without dissolving the oil and to form two layers: a treated oil layer substantially free from sludge and solvent, and a sub-

stantially oil-free solvent layer containing the sludge, and separating the layers.

3. In the process of refining a highly paraffinic lubricating oil by treating same with sulfuric acid under conditions to form a pepper sludge which is incapable of settling, the step of extracting the oil containing pepper sludge with a substantially oil-insoluble solvent containing at least 90% of a water soluble aliphatic oxy-hydrocarbon of not more than six carbon atoms under conditions to dissolve the pepper sludge substantially without dissolving the oil and to form two layers: a treated oil layer substantially free from sludge and solvent, and a substantially oil-free solvent layer containing the sludge, and separating the layers.

4. In the process of refining a highly paraffinic lubricating oil by treating same with sulfuric acid under conditions to form a pepper sludge which is incapable of settling, the step of extracting the oil containing pepper sludge with a substantially oil-insoluble solvent containing at least 90% acetone under conditions to dissolve the pepper sludge substantially without dissolving the oil and to form two layers: a treated oil layer substantially free from sludge and solvent, and a substantially oil-free solvent layer containing the sludge, and separating the layers.

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