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OXIDATION REFINING OF LUBRICATING OIL

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This invention relates to the refining of lubricating oils by means of oxidation, particularly for the purpose of improving the viscosity index of the lubricating oils.

It has been proposed in the past to refine lubricating oil stocks by means of oxidation with air, oxygen, ozone, etc. for various purposes, such as improvement of sludge stability, improvement of color, removal of volatile materials, etc. These prior processes have related to very mild oxidations which remove only a very small amount of the most highly reactive constituents of the lubricating oil stock. I have found that certain new and unexpected results can be attained by much more drastic oxidation. I have found that one of the principal effects of this more drastic oxidation is a very marked and important improvement in the viscosity index (Dean and Davis, Chemical and Metallurgical Engineering, volume 36, 1929, page 618) or, in other words, in the temperature coefficient of viscosity of the lubricating oil. It appears that the first materials to be oxidized are those of low viscosity index which are the least valuable and most objectionable constituents of the lubricating oil. I carry my oxidation to the point where a large portion of the oil is oxidized and a very marked improvement in viscosity index occurs, as will hereafter become apparent. The oxidized oils are then processed to remove the oxidation products and can undergo such further refining steps as acid treating, solvent extraction, clay treating, etc. to yield a lubricating oil product markedly superior to products produced without the steps of drastic oxidation and removal of the oxidation products.

It is an object of my invention to provide a process for the production of improved lubricating oils by drastic oxidation of a lubricating oil stock. It is a further object of my invention to provide a process of this type for improving the viscosity index of lubricating oils. Another object is to provide an oxidation process of an improved type using certain oxidation catalysts. Still another object of my invention is to provide certain combination processes using the steps of oxidation and removal of oxidation products in conjunction with other refining steps to give new and improved lubricating oil products. Other and more detailed objects of my invention will become apparent as the description thereof proceeds.

It would naturally be expected that in the drastic oxidation of a lubricating oil stock the most readily oxidizable materials would be destroyed to yield a product which was very resistant to oxidation. This, however, is not the case, particularly when oil soluble oxidation products are not completely removed. Thus, it has been found that when a Mid-Continent lubricating oil distillate having a viscosity at 210° F. of 120 seconds Saybolt is treated with three times its own volume of beta beta' dichlordiethyl ether at 100° F., the solvent removed from the raffinate and the raffinate treated with Attapulgus clay in the amount of one ton per 275 gallons of oil, the resulting oil requires 100 hours in the Indiana oxidation test (National Petroleum News September 13, 1933, page 30) to form 10 mgs. of sludge per 10 grams of oil. In comparison, when a sample of this same lubricating oil distillate was oxidized by bubbling air through it for 16½ hours at a temperature of 450° F. to 475° F. and then submitted to an identical treatment with beta beta' dichlordiethyl ether and a treatment with a much greater quantity, namely, one ton per 250 gallons, of the identical clay, the corresponding time required for the formation of 10 mgs. of sludge in the Indiana oxidation test was only 25 hours. Thus, in the second case using the oxidized distillate the final product was very much less stable to oxidation than was the product of the process using the unoxidized distillate in spite of the fact that in the former case a much larger quantity of clay was used which would normally tend to greatly improve the oxidation stability.

Thus, drastic oxidation alone does not improve the oxidation stability, but, in fact has the opposite effect. Nevertheless, this drastic oxidation is highly beneficial, principally with reference to the improvement in viscosity index. This is particularly true if the oxidation products are carefully removed following the oxidation step. Thus, for example, when a dewaxed Mid-Continent lubricating oil distillate having an S. A. E. number of 50 was oxidized by blowing air therethrough for about 11½ hours at a temperature of 450–475° F. (equivalent to about 65 hours in the Indiana oxidation test at 340° F.) and the resulting oil was distilled over solid sodium hydroxide under a vacuum corresponding to a distillation pressure of from 4 to 8 mm. of mercury, the resulting distillate had a viscosity at 100° F. of 1017 seconds Saybolt and at 210° F. of 79.9 seconds Saybolt, or in other words a viscosity index of 73. When a sample of the original lubricating oil distillate was vacuum distilled to give a distillate having approximately the same viscosity at 210° F. as the product of

the oxidation and distillation over sodium hydroxide above referred to, the viscosity index was found to be 54. In other words, the oxidation and removal of the oxidation products gave an improvement of 19 Dean and Davis viscosity index units. The oxidized oil contained several per cent of oil insoluble materials and was dark black in color while the final vacuum distillate using solid sodium hydroxide was free from oil insoluble materials and was relatively light-colored (5–6 N. P. A.).

The oxidation step contemplated by my process can be conducted in various ways. Commonly, the oxidizing agent used will be air, but oxygen, ozone and other oxidizing agents can be utilized. The oxidation can be conducted in a batch process by merely blowing or bubbling the oxidizing gas through it or it can be conducted in a tower or other continuous process. Thus, for example, the oil can be flowed down through a baffled or packed tower and the gaseous oxidizing agent can be passed upwardly through the same tower, the product being removed at the bottom of the tower. Various temperatures can be used, for instance, temperatures ranging from 200° F. or even less, up to 500° F. or any temperature below the temperature at which incipient local cracking is likely to occur. The temperature, of course, depends somewhat on the nature of the oxidizing agent used and low temperatures can be compensated for by long times of contact between the oxidizing agent and the oil undergoing oxidation. For purposes of reference, the degree of oxidation which I prefer can best be stated in terms of the Indiana oxidation test hereinbefore referred to. In this test, oil is subjected to oxidation with air under prescribed conditions at 340° F. and the sludge formed is measured at various stages during the oxidation. I prefer that the oxidation in my process be equivalent, in terms of the amount of sludge formed, to at least 50 hours and still more preferable to at least 100 hours under the conditions of the Indiana oxidation test. Oxidation times equivalent to as high as 500 or even 1000 hours in the Indiana oxidation test can suitably be used. As another means of stating the degree of oxidation contemplated by my invention, I prefer to use an oxidation sufficiently drastic to improve the viscosity index of the oil produced by my drastic oxidation and removal of the oxidation products by at least 15 and preferably at least 25 Dean and Davis viscosity index units as compared with an oil of similar voscosity at 210° F. produced by reduction of the original lubricating oil stock. Still otherwise stated, I prefer to use an oxidation sufficiently drastic to convert at least 20% by weight and preferably at least 35% by weight of the original lubricating oil stock into oxidation products.

I also find that the time necessary for oxidation in my process can be greatly reduced at the same time accomplishing the same results in terms of the Indiana oxidation test by utilizing a small amount of an oxidation catalyst. Various catalysts can be used, some of which are listed below. The oil soluble polycarbocyclic hydrocarbons and their derivatives are useful as a class.

In order to illustrate the effect of my oxidation catalysts, I have compared them in the Indiana oxidation test with a control oil containing no catalyst. This control oil required 29 hours in the Indiana oxidation test to produce 10 mgs. of sludge per 10 grams of oil and required 45 hours to produce 100 mgs. of sludge per 10 grams of oil. As compared with these results the following table gives corresponding times to produce corresponding amounts of sludge in oils containing the indicated weight percentage of various oxidation catalysts.

Per-cent	Catalyst	10 mg. sludge	100 mg. sludge
		Hours	*Hours*
0.2	Oleic acid	17	31
0.2	Sodium naphthenate	14	23
0.1	Tolidine	18	33
0.05	Thiodiphenylamine	13	32
0.1	Nitrosothymol	13	33
0.3	Sodium cyclohexanone	15	25
2.0	Phenanthrene	19	35
2.0	Acenaphthene	17	31
0.2	Sodium naphthylate	18	33

Not only is it important in order to produce a superior high viscosity lubricating oil that the oxidation be highly drastic as indicated above but it is also necessary that the oxidation products be removed as completely as possible. One way in which this can be done is by vacuum distillation and preferably by distillation under a high vacuum, for instance, distillation pressures of 8 mm. of mercury or less and preferably 4 mm. of mercury or less. The oxidation products are largely high boiling compounds and remain in the bottoms, but to some extent they pass over into the distillate and to that extent detract from the desirable characteristics of the distillate oil. I have found that this can be prevented by distillation over caustic, for instance, by placing a substantial quantity of a hydroxide or carbonate of an alkali or alkaline earth metal in the oil undergoing distillation or in the vapor space above the oil. I prefer to use sodium hydroxide and prefer to place it in the vapor space rather than in the liquid since only the distillate is thereby treated and waste of caustic prevented. The sodium hydroxide may be used in solid form or in molten form (for instance in a eutectic mixture with potassium hydroxide) or if steam is used in the distillation a very concentrated aqueous solution of caustic can be maintained. The use of caustic is very effective since many of the oxidation products are either acid materials or tend to decompose into acid materials when subjected to the elevated temperatures necessary to effect distillation even under vacuum. The caustic removes oil soluble oxidation products and thereby tends to improve sludge stability as well as viscosity index.

The product resulting from the drastic oxidation and removal of the oxidation products is a highly superior one from the standpoint of viscosity index but it does not have an altogether satisfactory oxidation stability and may be deficient in other respects. It is, therefore, desirable to follow these steps with other refining steps. Thus, for example, this intermediate product can be acid treated and clay treated in the normal fashion to give an oil highly superior, not only from the standpoint of viscosity index but also from the standpoint of sludge stability, color and other properties. As an illustration, a dewaxed Mid-Continent lubricating oil distillate having an S. A. E. number of 50 was oxidized by blowing with air for 11½ hours at a temperature of 450–475° F. and the oxidation products were then removed as a bottoms by distillation at a pressure of 4 to 8 mm. of mercury. The distillate was then treated with one pound per gallon of 91% sulfuric acid, washed, and percolated

through 15% of its weight of Attapulgus clay. The viscosity index of the resulting oil was 79 compared with 54 for a reduced sample of the original stock having a comparable viscosity at 210° F. The color was improved to 3½ N. P. A. as compared with 8 N. P. A. for the reduced sample from the original stock. At the same time, the oxidation stability in terms of the Indiana oxidation test was very greatly improved, the sludge time being 62 hours to produce 10 mgs. and 83 hours to produce 100 mgs.

The intermediate product formed by oxidation and removal of the oxidation products can also be subjected with advantage to solvent extraction processes using any of the known solvents. Thus, for example, a sample of the vacuum distillate following the oxidation step described in the last paragraph was treated with two times its volume of beta beta' dichlordiethyl ether at 60° F. and the raffinate after removal of solvent was percolated, as in the preceding case, through 15% of Attapulgus clay, the resulting product having a better viscosity index but a lower sludge stability than in the case of the acid treated material. The viscosity index in the case of the solvent extracted product was 86. The color was again 3½ N. P. A. and the sludge times were 31 hours for 10 mgs., 63 hours for 100 mgs.

It will be noted that the examples given in the last two paragraphs removed oxidation products by means of vacuum distillation without caustic. I have found that the more completely these oxidation products are removed, the more efficacious are the subsequent refining steps. Thus, for instance, in a process otherwise identical with the one described in the last paragraph, the vacuum distillation was conducted at the same pressure but in the presence of solid sodium hydroxide. The final product after solvent extraction and clay treating under identical conditions had a viscosity index of 93 as compared with 86 in the preceding example, a sludge time of 43 hours as compared with 31 hours in the preceding example and a color of 3 N. P. A. as compared with 3½ N. P. A. in the preceding example.

It is also obvious that acid treating or solvent extraction can be used alone or in combination with each other, either with or without the clay treating step and that the clay treating step can be used with or without acid treating or solvent extraction.

In any event the combination of distillation with or without caustic, to remove the bulk of the oxidation products followed by further treating as described to remove the final traces of oxidation products and improve the finished oil gives a highly economical and efficient process as compared with the direct treating of the oxidized oil without intermediate distillation.

My process is also advantageous for processing an undistilled lubricating oil stock such as a long residuum. Such a stock can be oxidized in accordance with my invention and then distilled to form an asphalt bottoms containing the bulk of the oxidation products. Thus the distillation step following the oxidation replaces the distillation step which would be necessary in producing the finished oil even if oxidation were not used.

While I have described my invention in connection with certain specific examples and certain theories of operation, it is to be understood that these are by way of illustration only and not by way of limitation and I do not wish to be bound thereby except to the scope of the appended claims in which I have endeavored to set forth the novel features inherent in my invention.

I claim:

1. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components comprising, contacting said stock with a gas containing free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 50 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 15 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products.

2. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components comprising, contacting said stock with a gas containing free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 50 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 15 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products in the presence of a substantial quantity of a substance selected from the group consisting of the hydroxides and carbonates of the alkali and alkaline earth metals.

3. A process according to claim 2 in which said substance is sodium hydroxide.

4. A process according to claim 2 in which said substance is contacted with the hot vapors in the distilling step.

5. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components and comprising, contacting said stock with a gas containing free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 100 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 15 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products in the presence of a substantial quantity of a substantially anhydrous substance selected from the group consisting of the hydroxides and carbonates of the alkali and alkaline earth metals.

6. A process according to claim 5 in which said substance is sodium hydroxide.

7. A process according to claim 5 in which said substance is contacted with the hot vapors in the distilling step.

8. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components comprising, contacting said stock with a gas con-

taining free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 50 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 25 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products.

9. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components comprising, contacting said stock with a gas containing free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 50 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 25 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products in the presence of a substantial quantity of a substance selected from the group consisting of the hydroxides and carbonates of the alkali and alkaline earth metals.

10. A process for the refining of a lubricating oil stock containing both low viscosity index components and high viscosity index components and comprising, contacting said stock with a gas containing free oxygen at a temperature of at least about 200° F., but below the temperature at which incipient local cracking is likely to occur, for a time corresponding to at least about 50 hours' air blowing at 340° F., to convert into oxidation products a quantity of said low viscosity index components sufficient to effectuate an increase of at least 25 units in the viscosity index of the unconverted components as compared with the viscosity index of the stock, and vacuum distilling said unconverted components from said oxidation products in the presence of a substantial quantity of a substantially anhydrous substance selected from the group consisting of the hydroxides and carbonates of the alkali and alkaline earth metals.

BERNARD H. SHOEMAKER.

CERTIFICATE OF CORRECTION.

Patent No. 2,070,627. February 16, 1937

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 13, claim 10, for "50 hours'" read 100 hours'; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of March, A. D. 1937.

Henry Van Arsdale
Acting Commissioner of Patents.

(Seal)

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