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COAL ACID ESTERS AS SYNTHETIC LUBRICANTS

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This invention relates to synthetic lubricants and, more particularly, to lubricants derived from synthetic esters.

The reduction of the coefficient of friction between relatively moving surfaces in contact with each other, particularly metal surfaces, has long been a subject of study. Various lubricants have been used for this purpose but none has had the widespread adoption and use accorded to lubricants derived from petroleum. This is believed to be so because petroleum lubricants have an aggregation of properties adapting them for use for a wide variety of purposes, and furthermore petroleum lubricants are relatively cheap to prepare. Various synthetically derived lubricants have been suggested from time to time but they have not acquired widespread use, either because of their suitability for only certain specific uses or because of the fact that they are costly to prepare.

It is an object of this invention, therefore, to provide synthetic lubricants which may successfully be aplied to uses for which petroleum lubricants have heretofore been employed.

It is a further object of this invention to provide a synthetic lubricant that can be easily and cheaply prepared.

These and other objects are attained by the present invention wherein we provide as a lubricant for reducing the coefficient of friction between metal surfaces moving in contact with and relative to each other a film of a substantially neutral ester of a monohydric alcohol and the mixture of acids obtained by the oxidation with gaseous oxygen of an acqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke obtained by the carbonization of coal at temperatures below 700° C. For convenience, the acids described above are hereinafter referred to as "coal acids."

We have found that the substantially neutral monohydric alcohol esters of the mixture of coal acids described above provide excellent lubricants which may be employed for any application for which petroleum lubricants have heretofore been employed. These esters may be prepared economically and therefore do not suffer the high cost disadvantages of many prior art synthetic lubricants.

As has been stated, the acids used in the preparation of our synthetic lubricants are obtained by the oxidation with gaseous oxygen of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke obtained by the carbonization of coal at temperatures below 700° C. Suitable coals comprise anthracite, bituminous, sub-bituminous, lignite and other low grade coals. Suitable cokes are those produced by the carbonization of a coal at a temperature below 700° C., in a manner known to the art. If the cokes are produced at temperatures in excess of 700° C., they become graphitic and unsuitable for the production of coal acids in a satisfactory yield.

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The following is an example of the preparation of the coal acids.

Finely ground bituminous coal, alkali, such as sodium hydroxide, and water are mixed in a nickel-lined autoclave equipped with a turbomixer and with means for heating and cooling the charge. The amount of alkali used is in excess of that required completely to neutralize all of the coal acids formed in the oxidation process. By way of example, the proportions of the ingredients may be 15 pounds of coal, 15 gallons of water and 45 pounds of caustic soda. The charge is heated and then oxygen is bubbled therethrough. The temperature of the charge is maintained from 200° to 300° C. at a total pressure of from 500 to 1200 pounds per square inch. The reaction is exothermic and the temperature is maintained within the limits stated by cooling, such as by passing water through an internal cooling coil in the autoclave. The oxidation is continued until all of the carbonaceous material of the coal passes into solution and usually requires between 2 and 3 hours. Half of the carbon of the coal is oxidized to organic acids and the remainder to carbon dioxide. At the completion of the oxidation the charge is cooled to about 110° C. and is discharged from the autoclave. The ash of the coal, which is largely unattacked, is removed by filtering through a filter press.

The filtered product is an alkaline solution containing the sodium salts of the organic acids obtained by the oxidation of the coal. Enough sulfuric acid is added to this solution to liberate the free acids. Any insoluble material appearing after acidification with sulfuric acid is removed by filtering. The free coal acids obtained are water-soluble and may conveniently be obtained from their solution in water by extraction with a suitable water-immiscible organic solvent. Methyl ethyl ketone is a suitable solvent, since in the presence of the sodium sulfate produced by the acidification with sulfuric acid, methyl ethyl ketone is water-immiscible. The extract phase may then be transferred to a still for recovery of the bulk of the solvent, and the prod-

uct remaining in the still may then be fed to a vacuum rotary drier for removal of the remainder of the solvent. For convenience in subsequent handling, the dried product may be ground to a fine powder in a pebble mill.

The product obtained appears to be a mixture of aromatic acids. This mixture is a free-flowing yellow powder which is hygroscopic and substantially completely soluble in water. The average molecular weight of the acids is 250 and the average equivalent weight is 80. Accordingly, the average number of carboxyl groups per molecule is somewhat more than 3. The exact nature of the acids is unknown, but they are believed to contain tri- and tetra-carboxylic benzene acids, as well as acids having a more complex nucleus than the benzene ring.

In order to obtain the synthetic lubricants of our invention, the coal acids as obtained above are esterified with a monohydric alcohol to produce substantially neutral esters. Esterification may conveniently be carried out by refluxing 6 moles of the alcohol with 1 mole of the coal acids for several hours while continuously adding small amounts of anhydrous hydrogen chloride as a catalyst. Water is continuously removed from the reaction vessel until the theoretical amount of separated water indicates that reaction is complete. At this point any excess of the alcohol is allowed to distill out of the reaction vessel. Other methods of esterification may be employed, as will be understood in the art.

A wide variety of monohydric alcohols may be employed for the esterification. For example, the alkanols, particularly the straight chain alkanols containing up to 20 carbon atoms, such as methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, lauryl, myristyl, palmityl and eicosyl alcohols yield excellent products. Branched chain alkanols such as isopropyl alcohol, 2-ethyl-hexyl alcohol, and the like may also be employed. Other monohydric alcohols which may be employed are the unsaturated aliphatic alcohols such as allyl alcohol, crotonyl alcohol, oleyl alcohol and the like. Alicyclic and aromatic monohydric acohols such as cyclohexanol and benzyl alcohol are also suitable. Mixtures of monohydric alcohols may also be employed, particularly the mixture of alcohols obtained by the reduction of coconut oil fatty acids and known commercially as "Lorol," the mixture of higher molecular weight alcohols obtained as a byproduct in the synthesis of methanol from carbon monoxide and hydrogen, as well as the mixture of alcohols obtained as byproducts in the synthesis of hydrocarbons from carbon monoxide and hydrogen. A preferred sub-group of monohydric alcohols comprises the straight chain aliphatic alcohols containing from 4 to 12 carbon atoms.

If desired, the esters obtained as indicated above may be treated with lime and an absorbent, such as fuller's earth, to improve their properties. For example, in one such treatment the esters are stirred with 4 per cent by weight of fuller's earth and 4 per cent by weight of lime at a temperature of 150° to 200° C., and are then filtered. When this treatment was applied to the normal butyl esters, an increase in the viscosity index from 76 to 92 was obtained.

Representative properties of some of the esters of this invention are shown in the following table:

Ester	Initial B. P., °C. at 760 mm.	Sp. Gr.	Vis., SSU at 100° F.	Vis., SSU at 210° F.	VI	Pour Pt., °F.
n-Butyl (crude)	greater than 271	1.004 at 130°/60° F.	2,479	130	76	
n-Butyl (treated)[1]	greater than 271	1.143 at 130°/60° F.	10,210	360	92	
n-Octyl (crude)	greater than 360	1.0420 at 60°/60° F.	1,654	117	95	0
n-Octyl (treated)[1]	greater than 360	1.0420 at 60°/60° F.	1,820	123	94	0
n-Lauryl (crude)	greater than 306	0.9689 at 60°/60° F.	1,218	116	115	+53
n-Lauryl (treated)[1]	greater than 306	0.9689 at 60°/60° F.	1,267	120	116	+50

[1] Treated with fuller's earth and lime as disclosed in the preceding paragraph.

The esters of the coal acids obtained as described in the foregoing disclosure present a number of properties making them eminently suitable as lubricants. They have a high viscosity index. The high initial boiling points and extremely low vapor pressures of the esters, even at elevated temperatures, render any loss of these lubricants by vaporization under service conditions extremely remote. As a matter of fact, the esters of coal acids cannot be distilled in appreciable amounts by ordinary distillation techniques, and can only be partially fractionated by molecular distillation. The lubricants of our invention are very stable and thus may advantageously be used under conditions where oxidation and sludge formation of petroleum lubricants are likely to be encountered as, for example, when used as crank case lubricants for gasoline and diesel engines. Furthermore, the esters may be used in lieu of mineral oil for the compounding of lubricating greases by the compounding procedures known in the art. The esters also have excellent "oiliness" and pressure-carrying properties. For example, the lauryl ester of the coal acids was tested in the Falex Lubricant Testing Machine, and, for comparison, a good grade of a paraffinic petroleum lubricating oil was subjected to the same test. The following results show the marked improvement in wear and pressure-carrying properties resulting from our lubricants:

Lubricant	Teeth Wear in 3 Hrs., 100 lb. Load	Load at Seizure, Lbs.
Lauryl Ester of Coal Acids	2 to 3	1600 to 1700
Petroleum Lubricating Oil	8 to 16	800 to 1000

The Falex lubricant testing machine is essentially a device in which a small round standard pin is rotated between two standard alloy V-shaped bearing blocks. Suitable means for applying pressure to the blocks (thus putting pressure on the bearing surface) is provided by a large ratchet wheel which can be turned one tooth at a time up to the desired load.

The Falex wear test is conducted as follows: About 55 cc. of the lubricant to be tested is placed in an adjustable cup which is then raised so that the pin and V-blocks are completely immersed in the oil. The pin is started rotating at 290 R. P. M. and the ratchet wheel is turned up until a force of 50 pound on the bearing surface is indicated on a suitable gauge. Under these conditions, a break-in run of ½ hour is made. After the ½ hour break-in period, the ratchet wheel is further turned up until the bearing load is 100

pounds and the position of an index tooth of the ratchet wheel, relative to any fixed point near the periphery of the wheel, is noted. The test is continued for three more hours under these conditions, the load being held constant at 100 pounds by adjustment (turning up) of the ratchet wheel as the bearing surfaces are worn down. At the end of this three-hour period the test is stopped. The number of teeth which have been turned past the fixed reference point near the periphery of the ratchet wheel indicates the amount of wear that has occurred. The results of the test are reported as the "number of teeth," e. g. "5 teeth," "10 teeth," etc.

The Falex seizure test is run in the same machine, using the same amount of oil to surround the V-blocks and rotating pin as is used for the Falex wear test. Likewise the same speed of 290 R. P. M. is employed for the rotating pin. In the Falex seizure test a break-in period of ten minutes at a bearing load of 250 pounds is employed. At the end of the ten minutes break-in period at 250 pounds the bearing pressure is increased to 300 pounds and in regular 100 pound increments every three minutes thereafter until the pin "seizes" or until a maximum load of 2500 pounds is achieved. The "seize-point" is characterized by a sudden large increase of torque which can be seen on a torque indicator which is operated in conjunction with the rotating pin. The test result is expressed as the bearing load at which seizure occurs.

Although we have disclosed the use of our lubricants in lieu of mineral oils, the esters herein disclosed may be added to mineral lubricating oils in a minor proportion, say from about 0.1 to 20 per cent by weight, sufficient to confer one or more improved properties, such as retarding of rusting and improved oiliness and pressure-carrying properties, on the lubricating composition. Thus, for example, the addition of 20 per cent by weight of the lauryl ester disclosed herein to a mineral lubricating oil confers enhanced "oiliness" and pressure-carrying properties. When 0.1 per cent by weight of the lauryl ester was added to a mineral lubricating oil and the composition subjected to the ASTM corrosion test, designated ASTM D–665–44T, in the presence of distilled water, the composition passed the test, that is, there was no rust after 48 hours. The same mineral lubricating oil without the addition of the lauryl ester permitted heavy rusting after about 4 hours. We consider such improved mineral lubricating oil compositions containing the monohydric alcohol esters of the coal acids to be a part of our invention.

An outstanding advantage of the lubricants of our invention is that lubricants having properties desired for a specific application may be simply and economically prepared merely by varying the monohydric alcohol used for esterification of the coal acids. For example, the normal butyl esters of the coal acids make an excellent lubricant for transmissions, differentials and other gear type mechanisms where high viscosity and high load carrying capacity are required; whereas the lauryl esters of the coal acids make an excellent lubricant for internal combustion engines, such as gasoline and diesel engines.

What we claim is:

1. A process of reducing the coefficient of friction between metal surfaces moving in contact with and relative to each other which comprises lubricating said surfaces by a film of a substantially neutral ester of a monohydric alcohol and the mixture of aromatic acids obtained by the oxidation with gaseous oxygen at a temperature from about 200° to about 300° C. and at a pressure from about 500 to about 1200 pounds per square inch of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke obtained by the carbonization of coal at temperatures below 700° C., the acidification of the resulting alkaline solution to liberate said acids and the extraction of said acids with an organic water-immiscible solvent which will remove the acids.

2. The process of claim 1, wherein the monohydric alcohol is an alkanol containing up to 20 carbon atoms.

3. The process of claim 1, wherein the monohydric alcohol is a straight chain alkanol containing from 4 to 12 carbon atoms.

4. The process of claim 1, wherein the monohydric alcohol is butyl alcohol.

5. The process of claim 1, wherein the monohydric alcohol is octyl alcohol.

6. The process of claim 1, wherein the monohydric alcohol is lauryl alcohol.

7. The process of claim 1, wherein the carbonaceous material is finely divided bituminous coal.

8. A process for reducing the coefficient of friction between metal surfaces moving in contact with and relative to each other which comprises lubricating said surfaces by a film of a lubricant comprising a major amount of a mineral lubricating oil and a minor amount sufficient to retard rusting of a substantially neutral ester of a monohydric alcohol and the mixture of aromatic acids obtained by the oxidation with gaseous oxygen at a temperature from about 200° to about 300° C. and at a pressure from about 500 to about 1200 pounds per square inch of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke obtained by the carbonization of coal at temperatures below 700° C., the acidification of the resulting alkaline solution to liberate said acids and the extraction of said acids with an organic water-immiscible solvent which will remove the acids.

9. The process of claim 8, wherein the ester is added in an amount of from 0.1 to 20 per cent by weight of the mineral lubricating oil.

10. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, at least sufficient to retard rusting, of a substantially neutral ester of a monohydric alcohol and the mixture of aromatic acids obtained by the oxidation with gaseous oxygen at a temperature from about 200° to about 300° C. and at a pressure from about 500 to about 1200 pounds per square inch of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke obtained by the carbonization of coal at temperatures below 700° C., the acidification of the resulting alkaline solution to liberate said acids and the extraction of said acids with an organic water-immiscible solvent which will remove the acids.

11. The composition of claim 10, wherein the carbonaceous material is finely divided bituminous coal.

12. The composition of claim 10, wherein the monohydric alcohol is an alkanol containing up to 20 carbon atoms.

13. The composition of claim 10, wherein the monohydric alcohol is a straight chain alkanol containing from 4 to 12 carbon atoms.

14. The composition of claim 10, wherein the monohydric alcohol is butyl alcohol.

15. The composition of claim 10, wherein the monohydric alcohol is octyl alcohol.

16. The composition of claim 10, wherein the monohydric alcohol is lauryl alcohol.

17. The composition of claim 10, wherein the ester is added in an amount of from 0.1 to 20 per cent by weight of the lubricating oil.

18. A lubricant composition comprising a major amount of a mineral lubricating oil and from 0.1 to 20 per cent by weight on the oil of the substantially neutral ester of lauryl alcohol and the mixture of aromatic acids obtained by the oxidation with gaseous oxygen at a temperature from about 200° to about 300° C. and at a pressure from about 500 to about 1200 pounds per square inch of an aqueous alkaline slurry of finely divided bituminous coal, the acidification of the resulting alkaline solution to liberate said acids and the extraction of said acids with an organic water-immiscible solvent which will remove the acids.

19. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to retard rusting, of the substantially neutral ester of lauryl alcohol and the mixture of aromatic acids obtained by the oxidation with gaseous oxygen at a temperature from about 200° to about 300° C. and at a pressure from about 500 to 1200 pounds per square inch of an aqueous alkaline slurry of finely divided bituminous coal, the acidification of the resulting alkaline solution to liberate said acids and the extraction of said acids with an organic water-immiscible solvent which will remove the acids.

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