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COMPOUNDED LUBRICANT

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This invention relates to the provision of improved lubricating compositions consisting essentially of lubricating oils (e. g., hydrocarbon lubricating oils of mineral origin) containing dissolved therein substances functioning to enhance and improve the lubricating properties of said lubricating oils per se.

In U. S. Patent No. 2,096,390 to Arthur W. Burwell and Adolf Kempe there is described a lubricating composition consisting essentially of a solution, in a lubricating oil of mineral origin, of a small amount of a lubricity-improving mixture of aliphatic alcohol esters of saturated aliphatic hydroxy carboxylic acids derived from hydrocarbon mixtures such as petroleum fractions by the controlled, liquid-phase, partial oxidation of the latter by the Burwell process. According to that disclosure the hydrocarbonaceous starting material might be amorphous wax (i. e., "Sharples" wax) derived from petroleum, or paraffin wax, or a normally liquid fraction of petroleum such as, for example, a 36–40° Baumé petroleum distillate consisting chiefly of relatively high molecular weight aliphatic hydrocarbons; and the esterifying agent might be methanol, ethanol, propanol, butanol, isopropyl alcohol, secondary butyl alcohol, or other similar monohydric alcohol such as the relatively high molecular weight saturated aliphatic alcohols described in said Patent No. 2,096,390 as being co-formed in producing the petroleum acids from which said esters mixtures are prepared, or glycerin, or glycol, or ethylene glycol, or like esterifying agent. For preparing the aforesaid esters mixtures patentees might esterify the acids content of the crude oxidation reaction mixture without any separation of the acids (or of the eventual esters) from the other components of the crude mass, or they might, and preferably did, first effect a substantial separation of the petroleum acids from the other components of the crude mass and thereafter esterify the so-separated petroleum acids. In preparing the compounded lubricants patentees added the esters mixtures to lubricating oils of various sorts in amounts ranging between about 0.25% and about 2% (or even up to 4% or 6%) by weight.

It has been determined by repeated trials that the above described esters mixtures show a persistent although slight acidity. As normally produced in manufacture, the esters mixtures may have acid numbers of the order of 14. Their acid numbers may be materially lowered by washing them with dilute aqueous caustic soda solutions (e. g., with 3–5% NaOH). However, with such considerable amounts of water present, some dissociation of the esters proceeds, and hence the residual acidity is seldom reduced below an acid number of 8 by such washing treatment.

An object of the present invention is the provision of a lubricity-improving agent consisting essentially of alcohol esters of petroleum acids, which agent shall have an acid number not greater than 1. Another object of the invention is the provision of a neutralizing technic for substantially binding the residual acidity of the hereinbefore-described esters mixtures. Still another inventive object is to provide a lubricant composition consisting essentially of a solution, in a mineral lubricating oil, of a small amount of an oil-soluble mixture consisting mainly of alcohol esters of petroleum acids which solution shall be essentially neutral.

It has now been found that the residual acidity of the above referred to mixtures of alcohol esters of petroleum acids may advantageously be neutralized by treating the ester mixture, or a composition containing the ester mixture, with a suitable base (e. g., a basically-reacting compound of calcium or magnesium, such as the oxide, hydroxide, or carbonate thereof), and dehydrating whereby to convert the mixture's small content of petroleum acids into the corresponding stable metal salts—preferably into the corresponding stable alkaline earth metal salts (e. g., calcium or magnesium salts).

The resulting lubricity-improving products—which for brevity I call "limed esters" mixtures—are then mixtures consisting essentially of the aforesaid esters of petroleum acids and metal salts of petroleum acids, in which mixtures the esters very largely predominate, and whose acid number is not greater than 1 and may be made to be only a very small fraction of 1. Their contents of calcium as combined calcium are about equivalent to the acid numbers of the esters mixtures prior to liming. They show no staining on copper, brass, or iron. They are, in general, non-crystalline in character. When solidified from the liquid state they solidify as unitary masses, thereby distinguishing from the "non-limed" esters mixtures which latter generally solidify fractionally. They are, in general, completely soluble in mineral hydrocarbon oils, from gasoline to the heavier lubricating oil fractions. These "non-limed" esters mixtures which are normally fluid remain fluid after "liming" but are somewhat more viscous than their parent

mixtures—otherwise they have the same properties. The limed esters mixtures are equivalent to the unlimed esters mixtures in lubricity-improving properties and, of course, may be employed in any relation where the unlimed esters mixtures might be employed.

The "liming" treatment, according to the invention, comprises admixing milk of lime (or equivalent salt former) with the esters mixture, and heating the resulting mass, while agitating the same, at a temperature well above the boiling point of water for a time sufficient to dehydrate it thoroughly. In dehydrating, I prefer to heat the continuously agitated reaction mixture, at progressively elevated temperatures, to a top temperature of 235 to 250° F. I prefer to employ the milk of lime in excess (e. g., in an amount about twice the theoretical); therefore, after dehydrating the reaction mixture I filter it to remove excess lime and any other solids which may be present. In filtering, I may with advantage make use of a filter aid (e. g., inert infusorial earth, or equivalent).

This liming treatment is applicable to the esters mixtures derived from petroleum acids from oxidized paraffin wax or "Sharples" wax or neutral lubricating oils or other petroleum distillate fractions (including "kerosene," "fuel oil," etc.) from paraffinic or naphthenic or mixed paraffinic-naphthenic crudes. They may be esters of the lower molecular weight aliphatic alcohols (typified by methanol, ethanol, propanol, butanol, isopropyl alcohol, secondary butyl alcohol, etc.) or of the higher molecular weight aliphatic alcohols (typified by the alcohols co-produced when forming petroleum acids from mineral hydrocarbons mixtures by oxidation of the latter according to the Burwell process) or of such esterifying agents as glycerin, glycol, ethylene glycol and the like.

The "limed esters" mixtures are incorporated into lubricating oils in amounts ranging from 0.25% by weight up to 6% by weight, preferably from 0.75 to 2% by weight. The lubricating oils to be so modified may be dewaxed paraffinic lubricating oils, or dewaxed selective solvent-refined naphthenic lubricating oils, or dewaxed mixed-base lubricating oils, or conventionally refined oils of any sort. The lubricating oils may range between SAE 10 and SAE 70.

These limed esters mixtures are completely soluble in many lubricating oils. Solutions thereof in high viscosity index oils, however, frequently show some "haziness" due to the very small amounts of material of poor solubility. This "haze" may, if desired, be overcome by allowing the solution to settle, at room temperature, for 48 hours (more or less), mixing the same with an inert filter aid such as inert infusorial earth, and then filter-pressing through blotting paper or equivalent filtering material. The filtrate is brilliant, and remains brilliant over long-continued storage. The amount of haze-producing material removed by this treatment is so extremely small that no account of its loss need be taken in preparing the composition.

Illustrative of the compounded or blended fluid lubricant compositions of the present invention is a 1.5% solution of limed methyl esters of petroleum acids from paraffin wax in an airplane engine oil, of SAE 60, the latter being a low-cold-test dewaxed Pennsylvania base paraffinic oil having a viscosity of 120 at 210° F. This composition shows an acid number of 0.01. In contrast thereto a 1.5% solution, in the same oil, of the non-limed but otherwise identical esters mixture shows an acid number of 0.14.

As will be apparent from a consideration of the foregoing description, the invention is in no wise limited to the above illustrative example: the amount of dissolved limed esters mixture may be varied within the limits above set out; the solvent (that is, the lubricating oil) may be any commercially used mineral lubricating oil; the alcoholic residues of the esters may be other than methyl as above suggested; and the petroleum acids from which the esters were prepared may be those derived from other mineral hydrocarbon mixtures than paraffin wax. In general, I prefer so to compound the lubricant composition that the same shows an acid number not greater than about 0.02.

It is within the scope of my invention to form the substantially neutralized lubricity-improving ester mixtures in other manners than that specifically described above. Thus, I may form a solution or stable dispersion of the ester mixture in a lubricating oil and thereafter "lime" the esters content of the composition by treating the latter with the indicated amount of calcium hydroxide, dehydrating the whole composition by progressively heating the latter, while agitating it, to a top temperature of about 250° F., and removing solids by filtration. The "limed esters" composition so produced is the full equivalent of the composition prepared by dissolving in lubricating oil a pre-limed esters mixture.

Moreover, it is within the scope of the invention to effect the binding of residual acids of the esters mixtures with other basically acting materials than the milk of lime above mentioned. Thus, I may neutralize with calcium oxide or calcium carbonate or other suitable basically-acting compound of calcium, or I may neutralize with a basically-acting compound (e. g., the hydroxide, or oxide, or carbonate) of magnesium or barium or strontium or other alkaline earth metal, or with a basically acting compound of lithium, or even with a basically acting compound of lead, tin, zinc or another heavy metal other than aluminum, chromium, iron or other metal of the iron group. However, I prefer to employ either the calcium or the magnesium compounds for this purpose, since their soaps are outstandingly stable, insoluble in water, and yield very low total ash on ignition. Because the magnesium soaps are the full equivalent of the calcium soaps, I use the expression "limed esters" to cover the esters neutralized with magnesium compounds as well as those neutralized with calcium compounds. Use of a basically-acting compound of chromium or aluminum or of a basically acting compound of a metal of the iron group is excluded because the organic acid salts of these metals act as accelerators of oxidation of the lubricating oil; also, because they are, in general, so readily dissociated in the presence of water that their existence cannot be proved by ordinary titrometric methods.

I claim:

1. Process of preparing a substantially neutral lubricating oil addition agent, which comprises treating an oxidized petroleum fraction consisting essentially of alkyl esters of petroleum acids and a small amount of petroleum acids with an excess of a basically acting compound of an alkaline earth metal, at an elevated temperature above the boiling point of water, whereby to reduce the acid number to less than 1.

2. An improved lubricating oil addition agent consisting essentially of alkyl esters of petroleum acids with a small content of alkaline earth metal soaps of petroleum acids, said agent having an acid number less than 1 and being soluble in mineral lubricating oils.

3. An improved lubricating composition consisting of from 99.25 to 94% by weight of a mineral lubricating oil and from 0.75 to 6% by weight of an oil-soluble lubricating oil addition agent consisting essentially of alkyl esters of petroleum acids with a small content of alkaline earth metal soaps of petroleum acids, which addition agent has an acid number less than 1, said lubricating composition having an acid number not greater than about 0.02.

4. Process of preparing a substantially neutral lubricating oil addition agent, which comprises treating an oxidized petroleum fraction consisting of lower alkyl esters of petroleum acids and a small amount of petroleum acids, said esters mixture having an acid number of not to exceed about 14, with an excess of milk of lime, at an elevated temperature above the boiling point of water, whereby to reduce the acid number of the esters mixture to less than 1 and to dehydrate the resulting product, and removing unreacted excess lime from the dehydrated product.

5. An improved lubricating oil addition agent consisting essentially of lower alkyl esters of petroleum acids with a small content of calcium soaps of petroleum acids, said agent having an acid number less than 1 and being soluble in mineral lubricating oils.

6. An improved lubricating composition consisting of from 99.25 to 94% by weight of a mineral lubricating oil and from 0.75 to 6% by weight of an oil-soluble lubricating oil addition agent consisting essentially of lower alkyl esters of petroleum acids with a small content of calcium soaps of petroleum acids, which addition agent has an acid number less than 1, said lubricating composition having an acid number not greater than about 0.02.

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