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LUBRICATING OIL COMPOSITION

Vernon L. Ricketts, Oakland, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to an improved lubricating oil especially adapted for use in Diesel engines, dealing with mineral lubricating oils containing small quantities of a salt or salts of certain aromatic derivatives of higher fatty acids and metallic or amphoteric polyvalent elements.

It is known that Diesel engines place an extremely heavy burden on lubricating oils which are circulated through their internal lubricating systems during operation. Upon prolonged use of a lubricating oil in a Diesel engine, piston rings develop a tendency to stick, possibly due to the accumulation of products of oxidation such as tar, coke, etc., or for other reasons. Stuck piston rings cause blow-by and result in loss of power, waste of fuel, rapid destruction of the lubricating oil and damage to the engine.

In order to overcome piston ring sticking, small amounts of certain organic salts of calcium, such as described in the Vobach Patent 2,081,075, have been added to lubricating oils. It has been found, however, that the suitability and the effectiveness of compounds of this type vary with the aromatic grouping attached to the fatty acid radical of the salt, as well as with the metal which they contain. For instance, whereas the calcium salt of phenyl stearic acid is useful for the purpose, the corresponding salt of magnesium forms gels with mineral oils and is entirely unsuited. On the other hand as explained further on, if the phenyl group is not attached directly to the carbon chain of the fatty acid, but instead is linked thereto as a side branch through one or more intermediate aliphatic carbon atoms, acids are obtained, the magnesium and certain other salts of which are exceptionally effective as ring sticking inhibitors and do not cause gelling when used in the amounts required to inhibit piston ring sticking.

Accordingly I have discovered that compounds which are especially suited for inhibiting ring sticking and carbon deposition in Diesel engines comprise salts or salt-like compounds of polyvalent metallic and amphoteric elements, and more particularly the salts of light metals such as calcium, aluminum and especially magnesium of higher fatty acids, which acids have attached to their carbon chain an aromatic grouping as a side branch through an aliphatic link of one or more carbon atoms.

Higher fatty acids as herein defined are those which are substantially stable under conditions of lubrication, i. e., which do not polymerize or oxidize excessively to form resins, and which contain at least 10 carbon atoms, 12 to 22 carbons in straight chains being most desirable. The fatty acids may be saturated or mono-olefinic, and may contain substantially neutral substitution radicals such as OH radicals. Suitable fatty acids are for instance lauric, palmitic, stearic, arachidic, oleic, ricinoleic, etc., acids.

The aliphatic link which connects the aromatic grouping with the fatty acid carbon chain may be paraffinic or mono-olefinic and should contain preferably not more than 3 carbon atoms. It may advantageously, but not necessarily, be attached to the fatty acid carbon chain in close proximity, such as an alpha position, in regard to the carboxyl radical.

The aromatic grouping comprises hydrocarbon groups such as phenyl, naphthyl, tetra hydronaphthyl, anthracyl, etc., to which may be attached one or more alkyl radicals preferably of not more than 3 carbons each.

The general formula of my compounds is

$$R-C\begin{matrix} \diagup\!\!\!\!\diagup O \\ \diagdown OM \end{matrix}$$

where M is a polyvalent metallic or amphoteric element, preferably a light weight metal having a specific gravity below about 4; and R comprises an aliphatic carbon chain containing not more than one double bond and an aromatic hydrocarbon grouping attached thereto as a side branch through an aliphatic link of one or more carbon atoms, preferably in close proximity to the carboxyl radical.

My compounds may be obtained by reacting a higher fatty acid with an aromatic aldehyde under conditions to effect a condensation with simultaneous liberation of water. The general type of reaction involved may be illustrated as follows:

$$R_1CH_2COOH + R_2C\begin{matrix} \diagup\!\!\!\!\diagup O \\ \diagdown H \end{matrix} \longrightarrow R_1\underset{\underset{CHR_2}{\|}}{C}-COOH + H_2O$$

In this reaction I have indicated that the substitution takes place in alpha position to the carboxyl radical, the theory being that the carboxyl radical activates the alpha carbon. This, however, is not necessarily the case, and the condensation may take place at some other carbon atom particularly if the carbon chain contains a double bond and/or substitution radicals, which may activate other carbons of the chain and introduce factors affecting the relative reactivities of the several carbon atoms in an incalculable manner. Moreover when checking the degree of unsaturation of typical condensation products by means of iodine absorption, the theoretical degree of unsaturation was not always confirmed, and yet the acids so produced were equally as effective for ring sticking inhibiting purposes as the pure compounds which had condensed in accordance with the above equation and possessed the theoretical iodine numbers.

A typical example of producing one of the acids of my invention is as follows:

300 parts by weight of calcium stearate, 106 parts of benzaldehyde and 450 parts of acetic acid anhydride were heated to about 280° F. for 8 hours. The resulting mixture was then distilled at atmospheric pressure to remove acetic acid anhydride. The distillation residue was then treated with an excess of aqueous hydrochloric acid, and the upper layer containing alpha-benzalstearic acid was separated and washed with water to free it from acetic acid. The yield of alpha-benzalstearic acid was 75% of the theoretical.

If desired the double bond created by the condensation reaction may be reduced to yield a saturated bond. Thus the benzalstearic acid of the above example was dried, dissolved in absolute ethyl alcohol and treated with 100 parts metallic sodium at 130°–150° F. for three hours. After this, the benzalstearic acid was completely reduced to the equivalent benzyl compound.

The amounts of the salts herein described, required successfully to inhibit or retard ring sticking are quite small and usually vary between .5 and 2.5% of the lubricating oil, although smaller or larger amounts may be added.

As pointed out before one of the advantages of certain of my salts of my acids over similar salts of other aromatic fatty acids heretofore employed for ring sticking inhibition, resides in the fact that the salts of this invention produce non-gelling blended oils when added to hydrocarbon oils in ring sticking inhibiting quantities. Moreover, I have found that in general my salts are more soluble in hydrocarbon oils and less corrosive and/or abrasive than similar known salts.

When comparing the ring sticking inhibiting powers of the various polyvalent metallic, and amphoteric elements it was found that, in general, the power increases with decreasing molecular weights provided the stabilities of the salts are of approximately equal magnitudes. Thus, I have found that the salts of magnesium are better than those of aluminum, aluminum better than calcium, calcium better than barium, and so forth. For instance, whereas the magnesium and aluminum benzal stearates in quantities of about 1% of the lubricating oil inhibit ring sticking for over 1000 hours of continuous running, ring sticking has been known to occur with a lubricating oil containing a like amount of the calcium salt near 1000 hours of operation, and a heavier salt such as the barium salt, permitted occasional ring sticking after about 250 hours running of the engine. In the absence of any salt, ring sticking normally occurred in less than 100 hours under the standardized conditions of the tests.

The salts of boron and beryllium, though being highly effective for ring sticking inhibition, are less stable and subject to hydrolysis and for this reason are less desirable under conditions where hydrolysis may occur. Therefore the preferred group of compounds of this invention comprises the salts of the light metals, i. e., metals having specific gravities below about 4, and particularly the magnesium salts.

Besides the salts of the above polyvalent metallic and amphoteric elements, salts of Zn, Cr, Mn, Cu, Co and Pb are quite effective, their inhibiting powers in general decreasing with increasing atomic numbers of the metals. In some instances mixtures of several salts containing different metals have given very good results. Salts of the remaining metals not enumerated above are of less interest, either because they can be dissolved in mineral lubricating oils with extreme difficulty only, or because their ring sticking inhibiting powers, although positive, are insufficient for most practical purposes.

Lack of solubility can in many cases be overcome by the addition of mutual solvents such as alcohols, ethers, esters, fatty acids or similar polar compounds. For instance clear liquid solutions of lubricating oils containing 10 to 20% of magnesium salts of my acids were obtained in the presence of 10 to 20% excess of the free acids.

I have further found that it is not necessary for the successful inhibition of piston ring sticking and carbon deposition to add a finished salt of the product of reaction between a fatty acid and an aromatic aldehyde to the lubricating oil, but that it is sufficient to dissolve in the oil the several ingredients which under the conditions of lubrication will apparently combine to form the salts of my invention heretofore described. Thus whereas the salts of my invention may be produced by the interaction of aromatic aldehydes with higher fatty acids or their salts, and the salts so produced may be added to the lubricating oils, ring sticking has also been inhibited successfully by dissolving in the lubricating oil small quantities, preferably in approximate equimolal proportions, of a suitable fatty acid salt and an aromatic aldehyde.

Suitable aromatic aldehydes are, for instance, benzaldehyde, naphthaldehyde, anthracenealdehyde, tetrahydronaphthaldehyde, phenyl acetaldehyde, naphthacetaldehyde, phenyl propionic aldehyde, aldehydes in which the aromatic ring or rings contain alkyl radicals preferably of three or less carbon atoms such as toluyl aldehyde, xylyl aldehyde, propyl benzaldehyde, alkyl naphthaldehydes, etc. Instead of aldehydes I may employ chemically related substances, which upon oxidation are capable of yielding aldehydes; thus I may use the alcohols corresponding to the above aldehydes such as benzyl alcohols, naphthyl alcohols, etc., or esters of these alcohols, preferably with fatty acids, etc. For example, I have used a lubricating oil, which normally caused piston rings to stick in less than 100 hours running, for over 1000 hours continuous running by adding thereto sufficient equimolal amounts of magnesium stearate and benzyl alcohol or benzyl stearate to yield a theoretical quantity of 1.2% magnesium benzyl stearate. Likewise a lubricating oil containing 1.0% aluminum stearate and .7% benzyl stearate ran satisfactorily for over 1000 hours.

While I do not wish to be limited to any definite theories, I believe that the fatty acid and the aromatic aldehyde, or the compound capable of yielding such an aldehyde, combine under the lubricating conditions of internal combustion engines to form the aromatic fatty acid salts of my invention. However, whether or not the fatty acid salts and aromatic aldehydes, or compounds capable of forming aldehydes, which are independently dissolved in the oil, actually do combine to form the salts described earlier, is uncertain though likely. Therefore the expression "product of reaction of fatty acid and aromatic aldehydes" shall include any condensation product of such fatty acids and aromatic aldehydes formed before or during lubrication and shall also include the described aromatic fatty acids, even if produced by other processes than the one described in this specification but shall not include compounds in which an aromatic ring is directly attached to the carbon chain of a fatty acid.

The herein described salts, or compounds which upon reaction under lubricating conditions yield the salts, may be used in solution of any type of lubricant which is otherwise suitable for lubrication. Thus they may be blended with mineral lubricating oils prepared from paraffinic or non-paraffinic crudes, shale oils, coal tar distillates, etc., by distillation, hydrogenation and/or solvent extraction, or by polymerizing suitable olefines. If desired suitable lubricating oils may be compounded with fatty oils, various oiliness or extreme pressure compounds, corrosion inhibitors, etc.

I claim as my invention:

1. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of a salt combining an element selected from the group consisting of polyvalent metallic and amphoteric elements, with a higher fatty acid having not more than one double bond in the carbon chain to which is attached an aromatic hydrocarbon radical as a side branch through a link of one or more aliphatic carbon atoms said small amount being sufficient to inhibit ring sticking when the said composition is used in internal combustion engines.

2. A liquid lubricating oil composition comprising a mineral lubricating oil, and a small amount of a salt combining an element selected from the group consisting of polyvalent metallic and amphoteric elements, with a higher saturated fatty acid to which is attached an aromatic hydrocarbon radical in alpha position as a side branch through a link consisting of one to three aliphatic carbon atoms said small amount being sufficient to inhibit ring sticking when the said composition is used in internal combustion engines.

3. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of a salt of a polyvalent light metal and an aromatic higher fatty acid having not more than one double bond in the aliphatic carbon chain to which the aromatic radical is linked as a side branch to the fatty acid chain through a link of one or more aliphatic carbon atoms said small amount being sufficient to inhibit ring sticking when the said composition is used in internal combustion engines.

4. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of a magnesium salt of a higher fatty acid having not more than one double bond in the carbon chain to which is attached an aromatic hydrocarbon radical as a side branch through a link consisting of one to three aliphatic carbon atoms said small amount being sufficient to inhibit ring sticking when the said composition is used in nternal combuston engines.

5. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of magnesium alpha benzal stearate said small amount being sufficient to inhibit ring sticking when the said composition is used in internal combustion engines.

6. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of aluminum alpha benzal stearate said small amount being sufficient to inhibit ring sticking when the said composition is used in internal internal combustion engines.

7. A liquid lubricating oil for internal combustion engines capable of retarding piston ring sticking comprising a mineral lubricating oil which contains from .5 to 2.5% of a salt combining an element selected from the group consisting of polyvalent and amphoteric elements with an aromatic higher fatty acid having not more than one double bond in the aliphatic carbon chain to which the aromatic radical is attached as a side branch to the fatty acid chain through a link of one or more aliphatic carbon atoms.

8. A liquid lubricating oil for internal combustion engines capable of retarding piston ring sticking comprising a mineral lubricating oil which contains from .5 to 2.5% of a salt of a polyvalent light metal and an aromatic higher fatty acid having not more than one double bond in the aliphatic carbon chain to which the aromatic radical is attached as a side branch to the fatty acid chain through a link of one or more aliphatic carbon atoms.

9. A liquid lubricating oil composition comprising a mineral lubricating oil containing small amounts of an aromatic aldehyde and a salt combining an element selected from the group consisting of polyvalent metallic and amphoteric elements with a higher fatty acid which contains not more than one double bond, said aldehyde being capable of forming a condensation product with said fatty acid under conditions of lubrication in internal combustion engines, said small amount being sufficient to inhibit ring sticking when the said composition is used in internal combustion engines.

10. The composition of claim 9 in which the aldehyde and the fatty acid salt are contained in the oil in approximate equimolal proportions.

11. The composition of claim 9 in which the element is magnesium.

12. A liquid lubricating oil composition comprising a mineral lubricating oil and a small amount of a salt combining an element selected from the group consisting of polyvalent metallic and amphoteric elements with an aromatic fatty acid produced by condensing a higher fatty acid having not more than one double bond in the aliphatic carbon chain and an aromatic aldehyde, said small amount being sufficient to inhibit ring sticking when said composition is used in an internal combustion engine.

VERNON L. RICKETTS.