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ANTI-RING-STICKING LUBRICANT

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11 Claims. (Cl. 252—34)

This invention is related to improved lubricating oils, and more particularly deals with mineral lubricating oils containing dissolved therein small amounts of oil-soluble metal salts capable of reducing ringsticking tendencies of the oil.

It is well known that in Diesel engines in particular, piston rings have a tendency to become stuck due to an accumulation of coke in the ring grooves. It is also known that the addition of oil-soluble detergents to the lubricating oil does in many instances reduce or even prevent such ringsticking. The class of detergents most active for this purpose are oil-soluble metal salts of carboxylic and sulfonic acids, such as soaps of fatty acids, chlorinated fatty acids, aromatic fatty acids, naphthenic acids, rosin acids, paraffin carboxylic acids (produced by oxidation of paraffin wax), mahogany acids, alkyl derivatives of benzoic or hydroxy benzoic acids and many others. Salts of polyvalent metals are in general most active, e. g., of Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Sb, Cr, Mn, Co, Ni, etc.

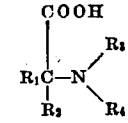
The addition of oil-soluble salts to lubricating oils in effective amounts, e. g., in amounts ranging from about .25% to 5.0%, however, introduces at the same time a number of difficulties, one of the most serious of which is bearing corrosion. Another is formation of hard coke, and still another is scratching of the top land of the piston.

The problem of corrosion seems to be very involved, corrosion apparently proceeding by at least one of several possible mechanisms with the effect that under some conditions an oil containing a dissolved salt may be non-corrosive and even a corrosion preventive, whereas under other conditions it may cause serious corrosion. Thus some oils containing a dissolved salt are initially corrosive, while others are initially non-corrosive but acquire induced corrosiveness, i. e., turn corrosive upon use under ordinary lubricating conditions as are encountered in internal combustion engines. In some instances corrosion has been reduced, though not usually altogether overcome, by the addition of various secondary dopes, such as anti-oxidants, anti-corrosives, etc. In this connection, it should be observed that in some instances the addition of secondary dopes has an effect contrary to what one should expect, i. e., cases are known in which, for example, a lubricating oil containing the combination of an oil-soluble salt and a proven commercial anti-corrosive are more corrosive than the same oil containing the salt alone.

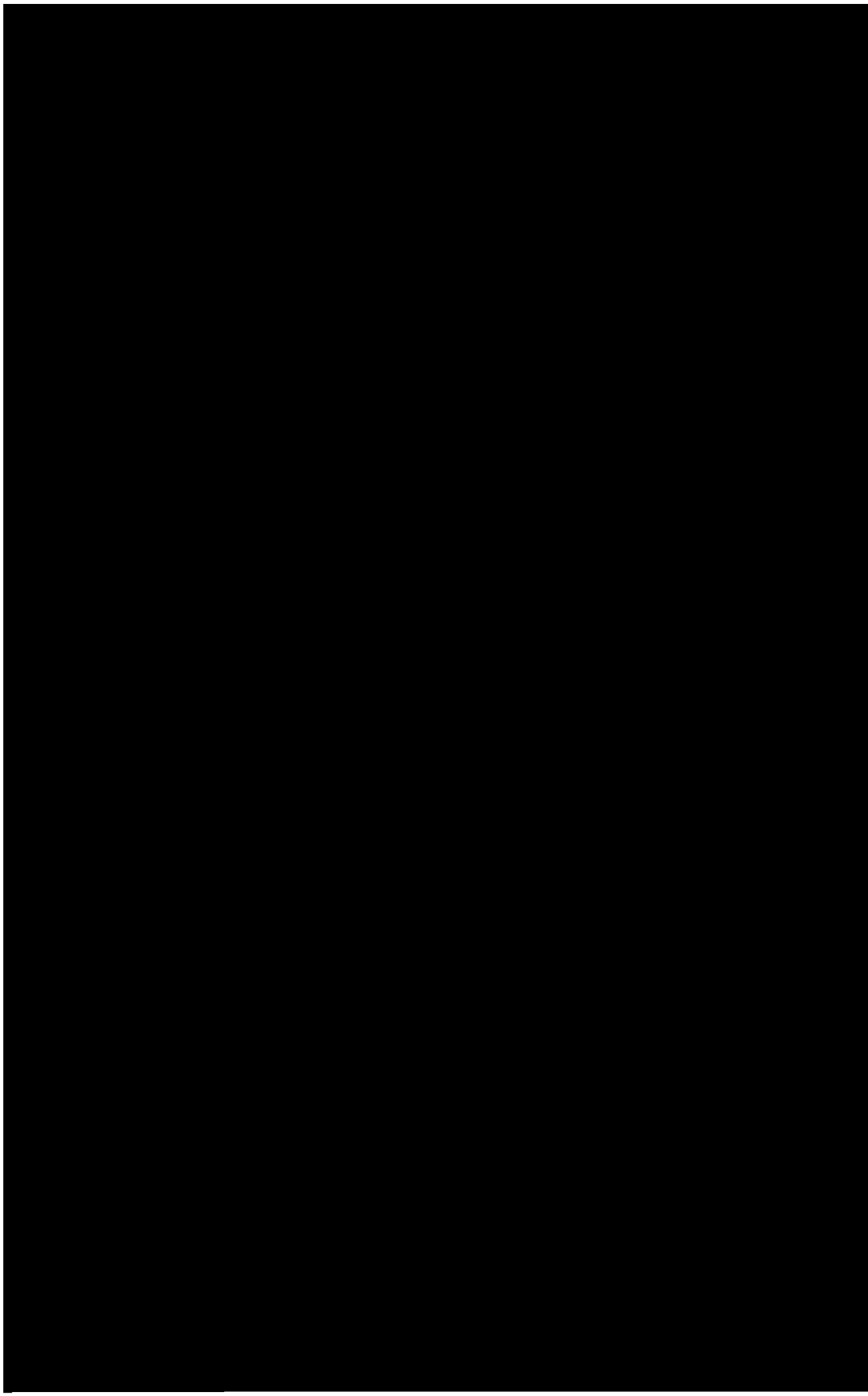
Among the detergents most valuable for anti-ringsticking purposes are the aliphatic carboxylic acids, e. g., fatty acids, aromatic fatty acids, naphthenic acids, paraffin carboxyl acids, rosin acids, etc. However, they all suffer from the common disadvantage of relatively high corrosiveness which may be initially active or be induced upon use.

It is a purpose of this invention to produce relatively non-corrosive lubricating oils suitable for internal combustion engines containing dissolved a detergent soap. It is another purpose to produce improved oil-soluble salts of aliphatic acids, which salts, when dissolved in mineral lubricating oils, combine an extraordinary degree of detergency with but little corrosiveness.

I have discovered that the corrosiveness of oil-soluble salts of aliphatic, alicyclic, aromatic carboxylic acids can be reduced materially and in many instances be suppressed to relatively harmless proportions by attaching an amino radical onto the carbon atom in the alpha position to the carboxyl radical. Thus the acids suitable for my purpose are amino acetic acid derivatives having the general formula



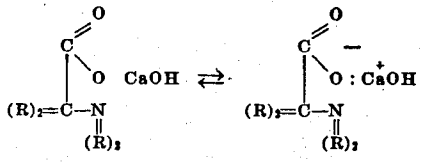
wherein R_1 to R_4 are hydrogen or hydrocarbon radicals which may be aliphatic, cyclic or alicyclic, at least one of them being a hydrocarbon radical, the total number of carbon atoms and their configuration in these radicals being such to result in an oil-soluble salt. As a general rule, not less than 16, and preferably 20 or more carbon atoms, are required in at least one of these radicals to confer oil-solubility on metal salts formed by these acids. The presence of naphthenic rings often results in greater solubility for a given number of carbon atoms. If desired, the R radicals may contain relatively



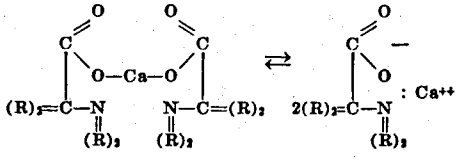
propyl, butyl, amyl, hexyl, allyl, etc., primary or secondary amines, petroleum bases (particularly from straight run petroleum oils), piperidine, pyrrolydine, pyrolene, pyrrol, ethylene diamine, propylene diamine, butylene diamine, primary or secondary ethanol-amine, aniline, mono alkyl anilines, such as methyl, ethyl, propyl, butyl, etc., anilines, toluidine, xylidines, diphenyl amine, naphthylamine, mono alkyl or aryl naphthyl amines, etc. The free alpha amino carboxylic acid is then converted to the metal salt by any of the conventional methods. Thus it may be directly reacted with an oxide or hydroxide of the desired metal, or its alkali metal salt may first be formed which is then double-decomposed with a suitable salt containing the desired metal.

Any of the metals heretofore known to be suitable for anti-ringsticking purposes may be used. From the point of view of detergent effect, the polyvalent metals, Mg, Ca, Ba, Zn, Al, Sn, Cr and Co are preferred. On the other hand, salts of metals having a strong tendency to form complex compounds, such as Cu, Ag, Ni, Co, Mn, Cr, etc., because of their preference to form chelates, are the least corrosive, as will be explained hereinafter. Either normal or basic salts or their mixtures may be used.

As already stated, salts of the alpha amino acids are less corrosive than the same salts of corresponding acids not containing the amino radical, or containing an amino radical in a position other than the alpha position. While I do not wish to be bound by my theory, I believe that the following is explanation for the improved behavior. It appears that at least one of the mechanisms by which corrosion proceeds is directly related to the electrical conductivity of the oil. Most oil-soluble salts, such as those heretofore used for imparting detergency to lubricating oils are slightly ionized in hydrocarbon oil solution, as a result of which the oil becomes conductive. However, salts of acids having a trivalent nitrogen in alpha position to the carboxyl radical exist in two forms which are in equilibrium with each other, namely, the chelate (inner ring) and the non-chelate forms. The latter ionizes, but the former does not. Thus the equilibrium may be illustrated as follows:



or



Chelate form ionized form

If a chelate form is the preferred one, relatively few ions can form, and the corrosion is accordingly reduced. Simultaneously, however, one would expect a similar reduction in detergent properties, because, as far as known, it is the ionized portion of the salt which is responsible for the detergent effect. However, the alpha amines do not show the expected detergency loss, and, on the contrary, often are materially better in this property than the same or similar salts of the corresponding acids not having the alpha amino radical.

This is believed to be due to the fact that certain definite but small amounts of ionized detergent salts display substantially as great dispersive action as larger amounts, while the corrosive property is more nearly proportional to the amounts of ions present. Thus, from the point of view of detergency of the oil, it is only necessary to have in the oil at any one time the minimum amounts of active ions which are just sufficient to disperse whatever sludge or sludge-like materials happen to be contained in the oil at that moment. As the dispersion proceeds, these minimum amounts are used up and the oil would be left unprotected, unless new active ions are introduced. Due to the presence of relatively large amounts of inactive detergent salts, effective quantities of these ions are quickly restored, and thus continued detergency of the oil is assured.

Concerning the equilibrium between the chelate and the non-chelate forms of the normal and basic salts, it appears that in the case of the normal salt the chelate is preferred, whereas in the basic salt the ionized form predominates. As a result, it has been found that the normal salts of the alpha amino acids are even less corrosive than the basic ones, whereas it was heretofore believed necessary that to suppress corrosiveness one must employ the basic salts.

The above peculiar reversal of the rate of corrosiveness as affected by alkalinity in the case of the alpha amino salts is of considerable importance. One of the main causes for the type of corrosiveness which is induced upon use of the oils containing detergent salts is believed to reside in a gradual reduction of the alkalinity of the salt with a commensurate decrease in the pH value due to oxidation. In the case of the alpha amino salts, however, the transition from the basic to the normal salt has just the opposite effect, corrosion decreasing for reasons pointed out above, rather than increasing.

In the normal salts of some of the alpha amino acids the equilibrium in favor of the chelates is so pronounced that an amount of detergent-active ions may be formed less than the minimum required for truly satisfactory detergency. In such cases it may be desirable to use a mixture of normal and basic salts so as to result in an oil solution containing the required minimum amount of ions; or a mixture of a normal alpha amino carboxylic acid salt with a detergent salt which is not subject to chelate formation, such as an ordinary oil-soluble naphthenate, sulfonate, aromatic fatty acid salt, paraffin wax carboxylic acid salt, etc., may be employed.

The following example serves to illustrate my invention: Stearic acid was halogenated by the Hell Volhard Zelinsky reaction under conditions to insure complete conversion of all the stearic acid to the corresponding alpha halo acid halide. The resulting product was hydrolyzed with warm water, and the halo acid thereby obtained was dried by solution in isopentane and subsequent crystallization. The alpha brom stearic acid, which had a melting point of 60° C., was then heated with two equivalents of piperidine for one hour at 120°–150° C. At this point, all of the halogen was determinable with silver nitrate.

The product was cooled and neutralized with dilute H_2SO_4, taken up in benzene, and the benzene layer separated from the aqueous piperidine sulfate.

The benzene layer was mixed with two equivalents of a thick freshly slacked lime paste and the mixture was distilled with addition of more benzene until no further water came overhead with the benzene. When dry, the residual benzene solution was filtered to remove excess lime, and the filtrate was evaporated to dryness.

The residue was a reddish yellow glassy substance which readily dissolved in hot oil.

A solution of 1.7% by weight of this material in an SAE 30 mineral lubricating oil was produced. The resulting blended lubricating oil was tested, and is compared in the table below with two recognized detergent salts for Diesel lubricating oils for corrosiveness and detergency.

In the corrosion test a hardened steel disc is made to rotate for 20 hours under constant pressure against 3 copper lead alloy bearings. The bearing assembly rests in a welded steel cup and is covered with the oil to be tested. During the test the temperature of the oil is maintained at 107° C. The bearings are weighed before and after the test, the difference in the weight representing the loss sustained during the test.

The detergency is measured by filtering a suspension of carbon black under standard conditions through a column placed in a glass tube, which column consists of 1 cm. layers of a sand separated from each other by pieces of filter paper. As the oil filters through this column, the carbon black is gradually filtered out and beginning at a certain point down the column, the oil is free from suspended carbon black. This point can readily be determined by visually examining the edges of the several filter papers. Those above this point have blackened edges, while those below it remain white. By counting the number of blackened papers, a direct measure for the detergency is obtained. Under the conditions of the test straight lubricating oils have detergency numbers of 1–2. The presence of 1–2% of a good detergent normally raises it to 6–8, and in exceptional cases to 9 or 10.

Detergent in S. A. E. 30 oil	Corrosion bearing loss Mg./sq. cm.	Detergency number
1.7% calcium alpha piperidine stearate	.3	9
1.7% calcium phenyl stearate	28.0	8

In addition to the detergents of this invention, the lubricating oils may contain conventional oxidation inhibitors or retarders, anti-corrosives, extreme pressure agents, particularly those containing at least one of the elements S, Cl and P in relatively stable form, so as not to cause corrosion, blooming agents, dyes, etc. The amounts of the detergent required to retard or prevent ringsticking normally varies betwen about .25% and 5%, and preferably from .75% to 2.5% by weight of the oil.

I claim as my invention:

1. Lubricating oil comprising mineral lubricating oil containing dissolved from .25%–5.0% of an oil-soluble polyvalent metal salt of an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines.

2. Lubricating oil comprising mineral lubricating oil containing dissolved a small amount of an oil-soluble salt combining a polyvalent metal with an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines.

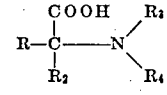
3. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble polyvalent metal salt of an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines, the amino radical of said acid being a secondary amino radical.

4. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble polyvalent salt of an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines, the amino radical of said acid being a tertiary amino radical.

5. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble mixture of basic and normal polyvalent metal salts of an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines.

6. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble mixture of a detergent salt not subject to chelate formation and of a polyvalent metal salt of an alpha amino acetic acid which is resistant to oxidation under normal lubricating conditions in internal combustion engines.

7. Lubricating oil comprising a mineral lubricating oil containing dissolved from .25 to 5.0% of an oil-soluble polyvalent metal salt of a monocarboxylic acid having not more than one olefinic double bond and having the formula



wherein R_1 to R_4 are hydrogen or hydrocarbon radicals, at least one being a hydrocarbon radical, the total number of carbon atoms in said radicals being at least 16 said salt being further characterized by being resistant to oxidation under normal lubricating conditions in internal combustion engines.

8. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble polyvalent metal salt of an alpha amino fatty acid having at least 16 carbon atoms and not more than one olefinic double bond, and having attached to the amino group at least one hydrocarbon radical.

9. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble polyvalent metal salt of an alpha amino naphthenic acid having attached to the amino group at least one hydrocarbon radical said salt being further characterized by being resistant to oxidation under normal lubricating conditions in internal combustion engines.

10. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of an oil-soluble polyvalent salt of an alpha amino paraffin wax monocarboxylic acid having attached to the amino group at least one hydrocarbon radical said salt being further characterized by being resistant to oxidation under normal lubricating conditions in internal combustion engines.

11. Lubricating oil comprising a mineral lubricating oil containing dissolved a small amount of calcium alpha piperidino stearate.

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