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ANTI-RING-STICKING LUBRICANT

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10 Claims. (Cl. 252—34)

This application is a continuation-in-part of my co-pending application, Serial No. 374,201, filed January 13, 1941.

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

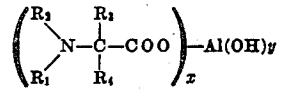
It is well known that in Diesel engines in particular piston rings have a tendency to become stuck due to an accumulation of coke in the ring grooves. It is also known that the addition of oil-soluble detergents to the lubricating oil does in many instances reduce or even prevent such ringsticking. A class of detergents most active for this purpose comprises 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 preventative, 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 the ordinary lubricating conditions that are encountered in internal combustion engines. In some instances corrosion has been reduced, though not usually altogether overcome, by the addition of various auxiliary agents, such as anti-oxidants, anti-corrosives, etc. In this connection, it should be observed that in some instances the addition of auxiliary agents 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 detergent salt and a proven commercial anti-corrosive are more corrosive than the same oil containing the salt alone.

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

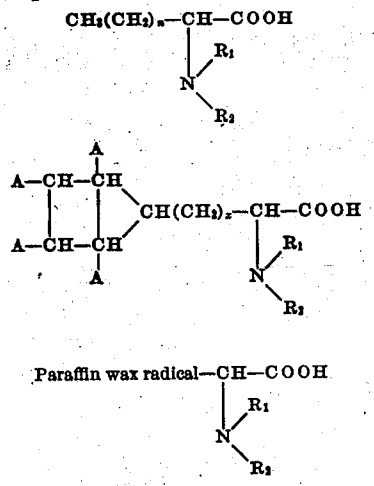
I have discovered that relatively non-corrosive lubricating oils of high detergency are produced by dissolving therein an oil-soluble aluminum salt of alpha-aromatic amino monocarboxylic acid of the general formula



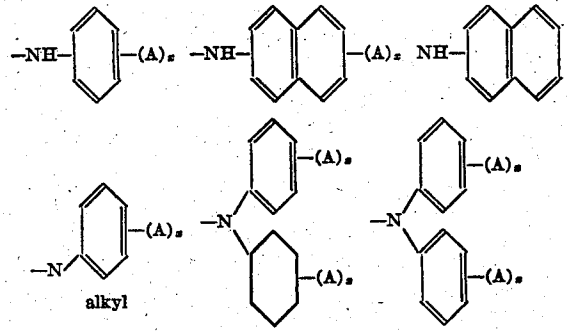
wherein R_1 is an aromatic hydrocarbon radical and R_2 and R_3 are hydrogen or hydrocarbon radicals and R_4 is a hydrocarbon radical, the total number of carbon atoms being such to result in an oil-soluble salt; and $x+y$ equals 3, x being at least 1. As a general rule, not less than 16, and preferably 20 or more carbon atoms are required in the acid to confer oil-solubility on the aluminum salt. 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 stable polar substitution radicals, such as halogen, hydroxyl, ether, hydrosulfide, sulfide, amine, imine, nitror, nitro, carboxylic ester, carboxyl, phosphorus, phosphite, phosphate, thiophosphate, arsine, etc. To be suitable for lubrication the acids should be relatively resistant to oxidation and therefore should not contain more than one olefinic double bond.

As may be seen from the above formula, the alpha amine radical may be secondary or tertiary. Among the acids meeting the above requirements are several which are particularly useful, e. g., alpha-anilino, -toluidino, -pyridino, -methyl anilino, etc., fatty acids, naphthenic acids or paraffin carboxylic acids totaling 22 or more carbon atoms and wherein the fatty acid chain contains at least 14 carbon atoms and not more than one olefinic double bond.

Thus acids of the following formulae are among the preferred:



In these formulae, n is an integer of at least 12, x is zero or an integer greater than zero, R_1 is an aromatic hydrocarbon radical probably mononuclear, and R_2 is hydrogen or a hydrocarbon radical. The A radicals are hydrogen or alkyl radicals (such as are contained in naphthenic acids naturally occurring in petroleum oils). Among the useful amino radicals are the following:

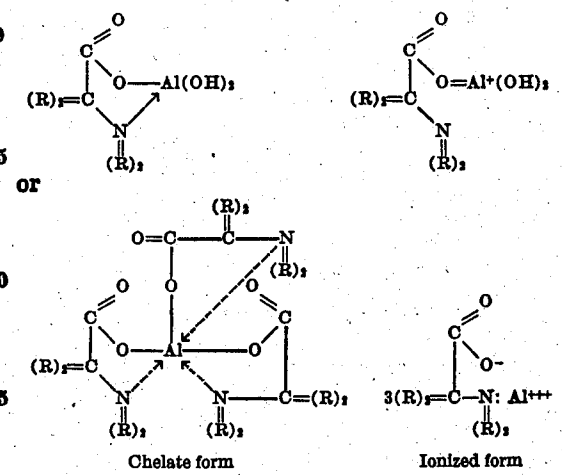


Aluminum salts of the alpha aromatic amino monocarboxylic acids of this invention have the advantage of being more oleophilic than the corresponding salts of acids not having the amino radical. This is of considerable advantage, as many of the readily available detergents, such as the polyvalent metal soaps of ordinary fatty acids, e. g., lauric, palmitic, stearic, arachic, behenic, etc., acids form unstable solutions in hydrocarbon oils, these soaps tending to precipitate from their solutions in the oils upon standing at ordinary room temperatures, thereby forming gels.

An alpha-aromatic amino monocarboxylic acid may be produced, for example, by starting with toluidino acetic acid and reacting it with a suitable alkyl halide containing, say, 16 or more carbon atoms such as chlorinated paraffin wax, etc.

Another method for producing alpha-aromatic amino monocarboxylic acids comprises halogenating aliphatic carboxylic acids under conditions to introduce at least one halogen atom in alpha position to the carboxyl radical. This may be accomplished by the Hell Volkard Zelinsky reaction (see Meyer and Jacobsen, vol. I, part 2, page 479) whereby an alpha halo acid halide is produced. This product is then hydrolyzed to liberate the alpha halo carboxylic acid. This acid is then simply heated, if necessary under pressure, with an aromatic amine. The free alpha-aromatic amino monocarboxylic acid is then converted to the metal salt by any conventional method. Thus, it may be directly reacted with an oxide or hydroxide of aluminum, or its alkali metal salt may first be formed which is then double-decomposed with a suitable salt containing aluminum.

As already stated, aluminum salts of alpha-aromatic amino monocarboxylic acids are less corrosive than the same salt 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 three-valent 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 form. The latter ionizes, but the former does not. Thus the equilibrium may be illustrated as follows:



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. This is believed to be due to the fact that certain definite but small amount 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 non-detergent chelates, 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

asic salts, it appears that in the case of the normal salt the chelate is preferred whereas in the asic salt the ionized form exists to a greater extent. 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 the 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 my 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 the amount of detergent-active ions formed may be less than the minimum required for truly satisfactory detergency. In such cases it may be desirable to use a basic salt or 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 aromatic amino monocarboxylic 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 brominated by the Hell Volhard Zelinsky reaction under conditions to insure complete conversion of all the stearic acid to the corresponding alpha bromo acid bromide. The resulting product was hydrolized with warm water, and the bromo 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 o-toluidine for one hour at 120°–150° C. At this point, all of the bromide was determinable with silver nitrate.

The product was cooled, filtered from toluidino hydrobromide and crystalized from glacial acetic acid.

The above product was reacted with ammonium hydroxide in alcohol solution to form the ammonium salt. The alcohol solution of this salt was then mixed with an alcohol solution of aluminum hydroxide, the mol ratio of acid to aluminum being 3 to 1, until a precipitate formed. The filtered and dried precipitate was a rubbery substance which readily dissolved in hot oil.

A solution of 1.7% by weight of this material in an S. A. E. 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 members 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
	120° C.	130° C.	
1.7% aluminum alpha toluidino stearate	5.4	7.5	11
1.7% calcium alpha toluidino stearate	.1	32.2	7
1.7% calcium phenyl stearate	12	40	8
1.7% aluminum a-toluidino stearate+25% phenylalphanaphthylamine	0	0	11

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 between 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 a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino monocarboxylic acid which contains a sufficient number of carbon atoms in the acid to make said salt oil-soluble and which is resistant to oxidation under normal lubricating conditions in internal combustion engines said amount being sufficient to reduce ringsticking.

2. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino monocarboxylic acid which contains a sufficient number of carbon atoms in the acid to make said salt oil-soluble and which is resistant to oxidation under normal lubricating conditions in internal combustion engines, the amino radical of said acid being a secondary amino radical said amount being sufficient to reduce ringsticking.

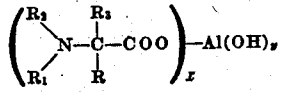
3. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino monocarboxylic acid which contains a sufficient number of carbon atoms in the acid to make said salt oil-soluble and which is resistant to oxidation under normal lubricating conditions in internal combustion engines, the amino radical of said acid being a tertiary amino radical said amount being sufficient to reduce ringsticking.

4. Lubricating oil comprising a mineral lubri-

cating oil and dissolved from .25% to 5% of an oil-soluble aluminum salt of an alpha-aromatic amino monocarboxylic acid which contains a sufficient number of carbon atoms in the acid to make said salt oil-soluble and which is resistant to oxidation under normal lubricating conditions in internal combustion engines.

5. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino fatty acid having at least 14 carbon atoms in the fatty acid chain and not more than a single olefinic double bond said amount being sufficient to reduce ringsticking.

6. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of a monocarboxylic acid having not more than one olefinic double bond and having the formula:



wherein R_1 is an aromatic hydrocarbon radical, R_2 and R_3 are hydrogen or hydrocarbon radicals, and R_4 is a hydrocarbon radical, the total number of carbon atoms being such to result in an oil-soluble salt, and $x+y$ equals 3, x being at least 1 said amount being sufficient to reduce ringsticking.

7. Lubricating oil comprising a mineral oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino paraffin wax monocarboxylic acid of at least 22 carbon atoms said amount being sufficient to reduce ringsticking.

8. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino paraffin wax monocarboxylic acid said amount being sufficient to reduce ringsticking.

9. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of an oil-soluble aluminum salt of an alpha-aromatic amino fatty acid of at least 16 carbon atoms and having not more than a single olefinic double bond said amount being sufficient to reduce ringsticking.

10. Lubricating oil comprising a mineral lubricating oil and dissolved a small amount of aluminum alpha toluidino stearate said amount being sufficient to reduce ringsticking.

ELLIS R. WHITE.