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RUST INHIBITOR FOR LUBRICATING OIL

Helen Sellei Beretvas, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to improved rust inhibiting compositions which are particularly useful in lubricating oils for internal combustion chamber engines.

Under normal operations of an internal combustion engine, wherein a lubricating oil is provided as a lubricating system separate and apart from the fuel system, the lubricating oil must function in the presence of water and air. Because of the presence of ferrous metal parts and because of the inability of the lubricating oil alone to give satisfactory rust inhibition, rust inhibiting addition agents must often be added to the lubricating oil. A particular rust problem results at corrosion sites created by acids introduced into the crankcase or oil reservoir from the combustion chamber by blow-by. The acids create corrosion sites by erosion of metal surfaces. Where such sites are cretted on ferrous metal surfaces, the eroded surfaces apparently become more susceptible to rust caused by the presence of water and oxygen. In low-speed short-time operation of an internal combustion engine, the accumulation of acids and water is increased and, it follows, the corrosion sites and rust at such corrosion sites are also increased. It has long been known that the lubricating oil alone is not sufficient to prevent rusting; this is particularly so with accelerated rusting at corrosion sites.

Rusting at corrosion sites is especially troublesome in a ne wengine. New engines are normally lubricated with a light lubricating oil known as a "drive-away" (break in or initial fill) oil. With a drive-away oil in the crankcase of a new engine, a new car is driven from the production line a short distance and then stored sometimes for extended periods of time. Blow-by acids from the combustion chamber accumulate in the crankcase and cause corrosion sites. During storage, water, e.g., from condensation, also collects and causes severe rusting especially at the corrosion sites.

I have now provided a mixture of ingredients which conjointly act to inhibit rust. The new mixture of ingredients is especially useful in internal combustion engine lubricating systems to prevent rusting, particularly at corrosion sitess. In a preferred embodiment of this invention, the mixture is used in internal combustion engine lubricating oils for drive-away purposes.

The mixture of conjointly acting ingredients, as provided by this invention, contains an acylsarcosine, a 1,2-disubstituted imidazoline and the reaction product of alkylene oxide and rosin amine (hereinafter referred to as "alkylene oxide-rosin amine"). The mixture of ingredients may be used in lubricating oils in minor amounts, in the presence or absence of other addition agents. It is preferred for use in internal combustion engines under normal operating conditions that the mixture of ingredients be included in the lubricating oil in an amount of from about 0.002 to about 10 weight percent. For use in light lubricating oils for drive-away purposes, it is advantageous that the mixture of ingredients be included in the lubricating oil in an amount of from about 0.1 to 2 weight percent and preferably 0.5 to 1.5 weight percent. Concentrates of the mixture of ingredients are also intended; such concentrates may contain the mixture of ingredients in amounts of from about 5 to 100 and preferably 30 to 70 weight percent, e.g. in suitable solvent such as a hydrocarbon, a low molecular weight alcohol, a monoalkyl ether of a glycol, e.g. Cellosolve, etc.

Although the proportions of each ingredient of the mixture of this invention may be varied by those skilled

in the art for particular purposes, it is advantageous that the weight ratio of the total acylsarcosine and imidazoline to alkylene oxide-rosin amine be in the range of from 50:1 to 1:1 and preferably in the range of 20:1 to 5:1. Advantageously, weight ratio of acylsarcosine to imidazoline may be from 0.1:1 to 10:1 and preferably from 3:7 to 7:3.

The acylsarcosine employed in the rust inhibiting composition is one which has the formula

$$RCON(CH_3)CH_2COOH$$

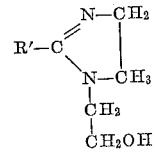
in which R is an alkyl radical having from 8 to 20 carbon atoms. The alkyl radical may be a saturated or unsaturated grouping having either a straight or branched chain. Because the primary purpose of the R grouping is to impart oil solubility to the acylsarcosine molecule, its particular configuration and the exact number of carbon atoms contained in the R grouping are not of critical importance, provided it imparts oil solubility. Mixtures of various acylsarcosine can be employed, or the individual acylsarcosines may be used. Those acylsarcosines whose alkyl radical is derived from a natural fatty acid composition are very satisfactory. For instance lauroyl-, stearoyl-, oleyl-, cocyl- (from cocoanut oil), sarcosines may be used.

The acylsarcosines may be prepared by reacting the desired acylchloride (having from 8 to 20 carbon atoms) with the alkali metal salt of methyl aminoacetic acid (requently methyl glycine or sarcosine) to form the alkali metal acylsarcosine which may then be partially hydrolized to the desired acylsarcosine. The reactions which occur may be illustrated as follows:

$$C_{11}H_{23}COCl + HN(CH_3)CH_2COONa \rightarrow C_{11}H_{23}CON(CH_3)CH_2COONa \rightarrow C_{11}H_{23}CON(CH_3)CH_2COOH$$

The acylchlorides which may be used are those suitably derived from natural fatty acid compositions such as have been discussed previously.

The 1,2-disubstituted imidazoline which is used corresponds to the following structural formula:



In the formula, R' represents a hlydrocarbon radical of 8 to 20 carbon atoms in length. It may be a saturated or unsaturated alkyl radical, having either a straight or branched chain. Since the primary function of the hydrocarbon radical represented by R' is to impart oil solubility to the molecule, the particular number of carbon atoms contained therein is not of critical importance.

The alkylene oxide-rosin amine used herein describes rosin amine-alkylene oxide reaction products. The rosin amines may be prepared by the reaction of stabilized gum and wood rosins with ammonia followed by catalytic hydrogenation at elevated pressure and temperature. The preparation is well known to the art. The rosin amines may contain both abietic-type amines and pimaric-type amines. The abietic-type amines include abietyl amine, levopimaryl amine, neoabietyl amine, dehydroabietyl amine, dihydroabietyl amine and tetraabietyl amine. The pimaric-type amines include dextropimaryl amine and isodextropimaryl amine. The alkylene oxide-rosin amines may be formed by the reaction of from 1 to 50 and preferably from 2 to 10 moles of a 2 to 3 carbon atom alkylene oxide, i.e., either ethylene oxide or propylene oxide with rosin amine. The alkylene oxide-rosin amines are believed to correspond to the formula

$$R''NH_x[(C_nH_{2n}O)_yCH_2CH_2OH]_z$$

wherein R'' is the residue of a rosin amine, e.g. an abietyl group, n is an integer of 2 to 3, x is 0 to 1, y is 0 to about 50 and preferably 1 to 9, z is 1 to 2 and the sum of x plus z is 2.

The alkylene oxide-rosin amines may be purchased if desired as commercial products. Examples of such commercial products are the alkylene oxide-rosin amines marketed under the trade name Polyrad by Hercules Powder Company. Such commercial akylene oxide-rosin amines vary in the alkylene oxide content apparently from less than one (on the average) to over 50 reacted alkylene oxide groups per average molecule. The Polyrads are ethylene oxide-rosin amine reaction products. The rosin amine used in their preparation predominates in abietyl amines such as dehydroabietyl amine and tetraabietyl amine. Alkylene oxide-rosin amines are marketed in concentrated form and in alcoholic solvent and may be used in either form. The alkylene oxide-rosin amines are normally solid and can be dissolved in alcohol if desired or can be utilized without solution in combination with the acylsarcosine and imidazoline for use in lubricating oils. An example of the Polyrads is Polyrad O515A which evidently has an average of about 3.6 reacted alkylene oxide groups per molecule calculated from nitrogen content.

The acylsarcosine and disubstituted imidazoline and alkylene oxide-rosin amine may be added separately or together to a lubricating oil. As a composition of matter, the three ingredients act conjointly to give improved rust inhibition. The lubricating oils which may be used are those normally used in the lubrication of internal combustion engines. Such lubricating oils include the mineral lubricating oils as well as other hydrocarbon oils both natural and synthetic, for example, those obtained by polymerization of olefins. The lubricating oil may also be those synthetic lubricating oils of the alkylene oxide type and the mono- and polycarboxylic acid ester-type, e.g., the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc. It is also contemplated that various other well known addition agents such as anti-oxidants, anti-foaming agents, pour point depressants, extreme pressure agents, anti-wear agents, dispersance or detergency agents, corrosion inhibitors, and the like may be incorporated in the lubricating oils containing the rust inhibiting ingredients of the present invention. The lubricating oils may be any such lubricating oils as described above but are not limited thereto. In the particular embodiment wherein the rust inhibiting ingredients of this invention are incorporated in a drive-away lubricating oil, it is advantageous that the lubricating oil may have an SAE grade in the range of 5 to 40 and preferably 10 to 30. In preparing the mixture of this invention the three ingredients may be added in any order although it is preferred to mix the acylsarcosine with the imidazoline and then add the alkylene oxide-rosin amine after the heat of reaction, if any, ceases. In this technique for preparing the synergistic mixture, it is believed that any neutralization reactability of the acylsarcosine and imidazoline is satisfied so that neither of these two components will subsequently react substantially with other addition agents which may be added to the lubricating oil composition or concentrate.

In order to demonstrate the utility of the mixture of ingredients of this invention, samples A through D were prepared as identified below and were tested in accordance with a modified HBr emulsion test. In accordance with that test, one inch by one inch polished steel squares were immersed in a 10% emulsion of 0.24% HBr in solvent extracted SAE 50 oil for one minute. The steel squares were then removed and suspended in the laboratory and exposed to the atmosphere for one minute. An exposed square was then dipped in each of samples A through D ten times within a period of one minute. The dipped squares were then suspended in the laboratory exposed to the atmosphere for two hours. The exposed squares were then placed in a humidity cabinet for 16 hours at 100% relative humidity and 100° F. After 16 hours, the squares were removed from the humidity cabinet and examined for percent of surface rusted. The result for each sample of oil tested is reported in Table I.

Sample A—An SAE 10 hydrocarbon lubricating oil containing 2.2 vol. percent of a metal neutralized phosphorus sulfide-hydrocarbon reaction product (detergency additive) and about 1.1 volume percent of a zinc dialkyl dithio-phosphate (corrosion and oxidation inhibitor).

Sample B—Sample A containing 0.1% of Polyrad O515A.

Sample C—Sample A containing 0.3% oleyl sarcosine and 0.3% 1-hydroxyethyl 2-heptadecenyl imidazoline.

Sample D—Sample C containing 0.1% of Polyrad O515A.

Table I

Sample:	Percent surface rusted
A	90 to 100
B	90 to 100
C	10 to 15
D	Less than 5

In order to further demonstrate the utility of the rust inhibiting combination of this invention, samples E, F and G, identified below, were each tested in accordance with the engine humidity storage test. The test procedure was as follows: for each sample tested, a Ford 6-cylinder engine was run for 25 minutes on leaded gasoline (3 cc. per gallon) with the crankcase filled to capacity with the oil sample being tested. After 25 minutes of engine operation, the engine was stored in a humidity room under the conditions indicated in Table II and for the length of time indicated in Table II. The engine was then inspected for percent of rust on the surface of the cylinder walls. The percent of rust was estimated from visual examination and was averaged among the cylinders and the average result is reported in Table II below:

Sample E—Sample A containing 0.5% oleyl sarcosine and 0.5% 1-hydroxyethyl 2-heptadecenyl imidazoline.

Sample F—Sample A containing 0.5% oleyl sarcosine, 0.5% 1-hydroxyethyl 2-heptadecenyl imidazoline and 0.1% Polyrad O515A.

Sample G—Sample A containing 0.35% oleyl sarcosine, 0.35% 1-hydroxyethyl 2-heptadecenyl imidazoline and 0.1% Polyrad O515A.

Table II

Sample	Test Conditions			Results—Percent Surface Rusted
	Percent Relative Humidity	° F.	Time, days	
E	[1] 65–95	[1] 85–95	[1] 4.5	45–50
F	60–66	92–100	5	5–6
G	65–83	87–95	5	[2] 5–8

[1] Run for 2.5 days at about 65% RH and about 85° F. and then for two days at about 95% RH and 95° F.
[2] Two runs.

With reference to the data reported above in Table I, it is seen that the alkylene oxide-rosin amine (Polyrad O515A) of sample B would not appreciably improve rust protection in the lubricating oil. Although the mixture acylsarcosine and 1,2-disubstituted imidazoline (sample C) would give good rust inhibition, the combination of alkylene oxide-rosin amine, acylsarcosine and imidazoline gave almost complete protection under the test conditions.

The data reported in Table II above again demonstrate the improved compositions of this invention (samples F and G,) in comparison with a mixture of acylsarcosine and 1,2-disubstituted imidazoline (sample E.) Using samples F and G as rust inhibiting compositions only,

from 5% to 8% rusting of the cylinder wall surface area was detected while 45% to 50% rust was detected using a greater percentage of sample E as the rust inhibitor.

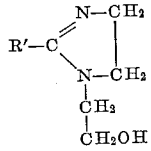
It is evident from the above that I have provided a new and improved rust inhibitor composition which is useful as a lubricating oil addition agent and which is especially useful in drive-away lubricating oils in new engines.

I claim:

1. A rust inhibitor composition comprising a rust inhibiting amount of a mixture of an acylsarcosine corresponding to the formula

$$RCON(CH_3)CH_2COOH$$

and a 1,2-disubstituted imidazoline corresponding to the formula



wherein R and R′ are alkyl radicals having 8–20 carbon atoms, and an alkylene oxide-rosin amine reaction product in an amount to further improve rust inhibition, said reaction product being formed by reacting 1 to 50 moles of a C_{2-3} alkylene oxide with rosin amine.

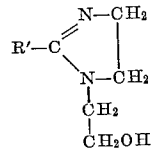
2. The composition of claim 1 wherein the weight ratio of said acylsarcosine plus said imidazoline to alkylene oxide-rosin amine reaction product is in the range of 50:1 to 1:1 and the weight ratio of acylsarcosine to imidazoline is 0.1:1.0.

3. The composition of claim 1 wherein the weight ratio of said acylsarcosine plus said imidazoline to alkylene oxide-rosin amine reaction product is in the range of from 20:1 to 5:1 and the weight ratio of acylsarcosine to imidazoline is in the range of 3.0:7.0 to 7.0:3.0.

4. The lubricant composition comprising a major amount of a lubricating oil and a rust inhibiting amount of a mixture of an acylsarcosine corresponding to the formula

$$RCON(CH_3)CH_2COOH$$

and a 1,2-disubstituted imidazoline corresponding to the formula



wherein R and R′ are alkyl radicals having 8–20 carbon atoms, and are alkylene oxide-rosin amine reaction product in an amount to further improve rust inhibition, said reaction product being formed by reacting 1–50 moles of a C_2–C_3 alkylene oxide with rosin amine.

5. The lubricant composition of claim 4 wherein the lubricating oil is a light lubricating oil having an SAE value of from 5 to 40 and capable of use as a drive-away oil in a new internal combustion engine.

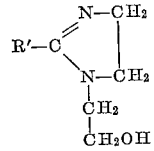
6. A lubricating oil addition agent concentrate comprising from 30 to 70% by weight hydrocarbon oil and from 70 to 30% by weight of the rust inhibiting composition of claim 1, said concentrate being capable of dilution with a lubricating oil to form a rust inhibited lubricant composition containing from about 0.002 to about 10 weight percent of said rust inhibiting composition.

7. A lubricant composition comprising a major amount of a normally liquid lubricating oil and from 0.1 to 2 weight percent of a mixture of oleyl sarcosine, 1-hydroxyethyl 2-heptadecenyl imidazoline and an ethylene oxide-rosin amine reaction product having an average of about 3.6 reacted ethylene oxide groups per molecule, the weight ratio of said acylsarcosine to imidazoline being from 0.1:1 to 10:1 and the weight ratio of total acylsarcosine plus imidazoline to said ethylene oxide-rosin amine reaction product being in the range of from 20:1 to 5:1.

8. The method for inhibiting rust in an internal combustion engine utilizing a crankcase lubricating oil, which method comprises contacting the engine with said lubricating oil containing a rust inhibiting amount of a mixture of an acylsarcosine corresponding to the formula

$$RCON(CH_3)CH_2COOH$$

and a 1,2-disubstituted imidazoline corresponding to the formula



wherein R and R′ are alkyl radicals having 8–20 carbon atoms, and an alkylene oxide-rosin amine reaction product in an amount to further improve rust inhibition, said reaction product being formed by reacting 1–50 moles of a C_2–C_3 alkylene oxide with rosin amine.

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