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3,000,916

COMPOSITION OF MATTER PREPARED BY REACTING POLYMERIZED LINOLEIC ACID WITH AN AMINE AND SUBSEQUENTLY REACTING THE MIXTURE WITH BORIC ACID

Donald L. Klass, Libertyville, Ill., and William L. Sieker, Crown Point, and Roger W. Watson, Highland, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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1 Claim. (Cl. 260—404.5)

This invention relates to a novel additive for inhibiting rusting of metals, and more particularly is concerned with providing an additive for engine lubricant oils for the purpose of inhibiting rusting in internal combustion engines. In another aspect, the invention provides a new composition of matter which has general utility as a rust inhibitor in hydrocarbon oil compositions.

Because of the wide variety of service conditions which automotive engines undergo, lubricant oils are required which are capable of providing complete engine protection not only for operation at high and sustained speeds, but for the urban type of driving. Although it might be expected that high speed driving with hot engines for long periods would impose the most stringent lubricant oil test, this is paradoxically not the case. Actually, the city driver who operates an automobile at low speeds, with a cold engine, is the one who requires special fortified grades of lubricant oils.

The reason for this apparent anomaly is that automobile operation with relatively cold engines results in the condensation of water, sulfur acids, and other corrosive combustion products on the cylinder walls. These condensates blow down past the piston rings and contaminate the crankcase oil, and hence engines in urban service may be using lubricant oils which contain considerable quantities of corrosive acids. In a relatively short period of time, a city driven automobile may be plagued by extensive rusting throughout the most important parts of the motor. Where engines have hydraulic valve lifters, this rusting can, within twenty or thirty hours of engine operation, cause valve lifters to stick, resulting in noisy and improper operation, and in severe cases immobilizing the engine. To protect against this, lubricant oils must be provided with additives which are especially tailored to inhibit the type of rusting which is due to city driving.

It is therefore a primary object of the instant invention to provide a novel composition of matter which is a superior rust inhibitor. A further object is to provide such composition which is exceptionally suited for preventing engine rusting in automobiles used in urban service. Another object is to provide an all-purpose anti-rust which is effective in widely different types of petroleum products. A special object is to provide a rust inhibitor composition for addition to lubricant oils which is also effective in preventing rusting of metal in contact with an aqueous phase which may separate out from the lubricant oil. Other and more particular objects will become evident as the description of the invention proceeds.

We have now discovered that a particular type of conventional lubricant additive, which is composed of the reaction product of an N-alkyl alkylene polyamine such as tallow-derived propylene diamine, and a polymeric long chain unsaturated polycarboxylic acid typified by dilinoleic acid, is vastly improved when the reaction product is borated by treatment with boric acid, boric anhydride (B_2O_3) or boric acid esters. The resulting composition is soluble in virtually all petroleum fractions in concentrations sufficient to impart effective rust inhibition to the oil. The novel additive composition of the invention may be prepared by first reacting an N-alkyl alkylene

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polyamine with a polymeric long chain unsaturated polybasic carboxylic acid, at a suitable temperature within the range of about 100 to about 300° F., preferably below about 225° F. The resulting salt is then borated with boric acid, boric anhydride, or a boric acid ester, either as a solid or in the presence of a solvent such as dioxane, acetone, or methanol. Since both the N-alkyl alkylene polyamine and the long chain carboxylic acid are each useful lubricant oil additives, the former as an anti-oxidant and the latter as an anti-rust, the proportions of these two are not critical, since any unreacted excess remains in the lubricant oil where it serves its own independent function. However, for optimum utilization of both the N-alkyl alkylene polyamine and the long chain polycarboxylic acid, it is preferred to use these in the proportion of from about 0.5 to 1.5 moles of diamine per equivalent of acid, more preferably from about 0.8 to about 1.2 moles per equivalent. The borating agent is also preferably used in a proportion of from about 0.8 to about 2.5 moles of boric acid (or other borating agent) per mole of diamine, with any excess either remaining with the additive or being removed therefrom. At the conclusion of the borating reaction, any inert solvent may be separated from the mass by steam or vacuum distillation. The final additive is preferentially oil soluble, but dissolves in water to a very slight extent which is sufficient, however, to inhibit rusting of iron or steel which is in contact with the aqueous phase.

Polymerized carboxylic acids such as dilinoleic and trilinoleic acids have particular value as the acidic component of the additive combination. Although the N-alkyl alkylene polyamines form salts readily with a wide variety of acids, the nature and size of the acidic component appear to be quite critical. The polycarboxylic acid must have at least two and preferably three free carboxylic acid groups for a high degree of effectiveness. In addition, it must possess a particular balance of solubility between oil and water phases. Additives formed with acids having a ratio of less than about 14–16 carbon atoms per carboxyl group are relatively water soluble and are leached too readily from oil solutions or are otherwise ineffective as light oil anti-rusts. Additives formed with acids containing more than about 60 carbon atoms per group appear to remain exclusively in the oil and fail to provide effective rust protection in the water phase. Although both dicarboxylic and tricarboxylic acids give excellent performance in protection against rusting in both oil and water phases, it appears that the tricarboxylic acids approach the optimum in this respect. The use of mixtures of polycarboxylic acids, such as may be derived by polymerization of unsaturated mono-acids, rather than pure acids reduces cost and appears to be advantageous in terms of function as well.

A very satisfactory acid for use in forming the new inhibitors is a mixture of polymerized fatty acids predominating in trilinoleic acid. A particularly satisfactory acid is commercially available from the Harchem Division of Wallace and Tiernan Co. under the tradename of D-50 Acid. A similar product is marketed by Rohm & Haas Company under the tradename VR-1 Acids. Such acids may be produced as by-product still-residues in the manufacture of sebacic acid by the distillation of castor oil (predominantly glyceryl triricinoleate) in the presence of caustic. A method of obtaining such by-product still-residues in the preparation of sebacic acid is described in U.S. 2,470,849 issued to W. E. Hanson May 24, 1949. The mixture of high molecular weight unsaturated fatty acids comprises monomers, dimers, trimers and higher polymers in the ratio of from about 45% to about 55% of a monomers and dimers fraction having a molecular weight in the range of from about 300 to 600,

and from about 45% to about 55% of a trimers and higher polymer fraction having a molecular weight in excess of 600. The fatty acid polymers result in part from a thermal polymerization of fatty acid type constituents of the castor oil, and in part from other reactions, such as the inter-molecular esterification of such acid to form high molecular weight products. The acid mixture, which is mainly a mixture of polymeric long chain polybasic carboxylic acids, is further characterized by the following specifications:

Acid No.....	150 to 164
Saponification No.....	175 to 186
Free fatty acids.....percent.....	75 to 82
Iodine value.....	44 to 55

Another useful, commercially available dimeric carboxylic acid is available from Emery Industries Inc. under the tradename Emery 955-Dimer Acid. Since the commercial product is produced by dimerization of linoleic acid ($C_{17}H_{31}COOH$), it is usually referred to as dilinoleic or dimer acid. The commercial acid typically contains about 85% of dilinoleic acid, about 12% of trilinoleic acid and about 3% of monomeric acid. Typical specifications for the commercial product are as follows:

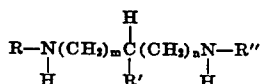
Iodine value.....	80-95.
Acid value.....	180-192.
Saponification value.....	185-195.
Unsaponifiable.....	2.0% max.
Color, Gardner.....	12 max.
Neutralization equivalent.....	290-310.
Refractive index at 25° C.....	1.4919.
Specific gravity at 15.5° C./15.5° C.....	0.95.
Flash point, ° F.....	530.
Fire point, ° F.....	600.
Viscosity at 25° C. (Gardner-Holdt).....	Z4.
Viscosity at 25° C., centistokes.....	10,000.
Viscosity at 100° C., centistokes.....	100.

A similar product from the same company is Emery 3065-S Polymerized Fatty Acid; a liquid made by polymerizing 18-carbon unsaturated fatty acids presumably linoleic acid. It is a mixture of about three parts of 36-carbon dibasic acid, one part of 54-carbon tribasic acid. Emery 3055-S is another similar product, apparently containing a larger amount of trimer acid.

Although the above are examples of commercially available mixed polycarboxylic acids, other polycarboxylic acids derived by polymerization of unsaturated acids and corresponding oil soluble polycarboxylic acid type materials, e.g. lecithin, also may be used.

For example, various naturally occurring or synthetic acids may be linked together to provide useful polycarboxylic acids by means well known to organic chemists, e.g. polymerization of unsaturated acids or condensation of alpha-halogenated acids, to produce polymeric forms of readily available carboxylic acids such as lauric, stearic, oleic, linoleic, oxo acids (e.g. isooctyl acids), synthol acids and the like.

Polybasic amines suitable for use in accordance herewith are the N-alkyl alkylene polyamines. Such amines, in general, may be represented by the structural formula:



wherein R represents an alkyl or substituted alkyl (i.e. by hydroxy, carboxy, nitro, halo-, etc. groups) hydrocarbon radical containing from about 16 to about 20 and preferably about 18 carbon atoms; R' may be hydrogen or an aliphatic hydrocarbon radical, i.e. alkyl or cycloalkyl radicals and it is preferably hydrogen; R'' may be hydrogen, an alkylene primary amine radical (i.e. $-(\text{CH}_2)_x\text{NH}_2$, wherein x is a positive integer from 1 to about 10) or a polyalkylene polyamino radical containing a primary amino nitrogen atom; m is a positive integer

from 1 to about 10 and preferably 1 or 2; and n may be either 0 or a positive integer from 1 to about 10. Typical examples of such compounds are the higher alkyl derivatives of ethylene diamine, of propylene diamines (1,3-diamino propane; 1,2-diamino propane), of diethylene triamine, of triethylene tetramine, etc.

More specifically, there may be employed such amines as N-octadecyl-ethylene diamine, N-n-cetadecyl diethylene triamine, N-n-cetylpropylene diamine, N-octadecyl triethylene tetramine, N-hydroxy octadecyl diethylene triamine, N-chloro-octylethylenediamine, N-bromo octadecyl ethylene diamine, Duomeens T, C, 12, and S (products of Armour Chemical Division) which have the general formula $\text{RNHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, wherein R is derived from tallow fatty acid ("Duomeen T"), from coconut fatty acid (Duomeen C) from lauric acid ("Duomeen 12") and from soya fatty acid ("Duomeen S") respectively, etc. The "Duomeens" are industrial or technical grade chemicals with an amine content of approximately 80% calculated as di-amine. The approximate melting ranges for some of the aforementioned "Duomeens" are: "Duomeen S"—38° to 42° C., and "Duomeen T"—44° to 48° C. It should be understood that the enumeration of the foregoing specific amino-compounds is by way of illustration and not of limitation and that any polyamine falling within the broad definition above recited may be employed in accordance herewith. The above enumeration is not, however, intended to imply equivalency for all purposes, and certain amines such as the N-alkyl propylene diamines appear to be superior to some of the other polyamines.

Lubricant oils, to which are added the composition of the invention, are petroleum-derived fractions having a Saybolt Universal viscosity of about 80 seconds or more at 100° F., and may conform with any appropriate lubricant oil classification specification. To provide effective rust inhibition, the additive is used in the lubricant oil at a concentration of from about 0.0001 to about 5 wt. percent, preferably between about 0.1 and about 2.0%. The oil may contain other ingredients such as viscosity index improvers, extreme pressure additives, bearing corrosion inhibitors and the like.

To more fully exemplify the various embodiments of the instant invention, the following non-limiting specific examples are set forth below.

EXAMPLE I

In this example, a typical additive of the present invention was prepared from a polymeric linoleic acid and a tallow-derived propylene diamine. The polymeric acid was Emery 955 Dimer acid, which is predominantly a dimer of linoleic acid, and has an average molecular weight (by titration with KOH) of 540. The diamine was Duomeen-T, having a combining molecular weight of about 400. 707 grams of dimeric acid (1.31 moles) and 943 grams (2.35 moles) of Duomeen-T were mixed together and heated with stirring at 221° F. for six hours. The reaction mixture was permitted to stand overnight without heating, and formed a rather hazy product. The boric acid was added as a suspension of 269 grams (4.35 moles) of boric acid in 450 ccs. methanol and the mixture stirred. 1065 grams of a hydrocarbon diluent oil was then added, and the entire reaction mixture stripped for four hours under 25 inch mercury vacuum at 176° F.

The borated product, hereinafter referred to as tallow amine-dimer acid-borate, was filtered through Celite and was in the form of a bright colored liquid, having a viscosity at 210° F. of 2495 SSU. By spectrometric analysis, it was found to contain 2.32 wt. percent nitrogen (2.21% calc.) and 2.0% boron (1.58% calc.). It contained 3.51% ash.

EXAMPLE II

This example illustrates the preparation of another

borated rust inhibitor composition. The acid was Hardesty D-50 acids, a commercial mixture of dilinoleic and trilinoleic acids and the diamine was Duomeen-T. 100 grams (0.29 moles) of Hardesty acids and 104.4 grams (0.26 moles) of Duomeen-T were stirred for six hours at about 221° F. in the presence of 205 grams of 5-W lubricating oil as an inert diluent. The reaction mixture was cooled and 37.11 grams (0.6 mole) of boric acid in 100 ml. of methanol was introduced. The mixture was heated to 212° F. and blown with nitrogen gas to remove methanol. The liquid was bright in color, requiring no filtration or other treatment, and contained 1.73% nitrogen, 0.96% boron, and 3.32% total ash.

EXAMPLE III

The tallow amine-dimer acid-borate prepared in Example I was tested under the conditions of the modified Indiana hydraulic valve lifter rust test. This test is an extremely severe, simulated service test which quantitatively measures the tendencies of lubricant oils to cause rusting of engine parts in automobile engines operated under urban driving conditions. In this series of runs, a standard solvent-extracted 5W-20 lubricant oil containing 4.25 wt. percent of barium neutralized hydrolyzed phosphorous sulfide-olefin polymer reaction product as a detergent, 1.2% zinc dialkyl-dithiophosphate oxidation inhibitor, and 5.5% Acryloid 794 (a methacrylate polymer viscosity index improver) was used. This oil, without any anti-rust, causes severe corrosion of the engine dip stick and rocker arm shafts, and extremely severe corrosion and sticking of the hydraulic valve lifters.

The modified Indiana hydraulic valve lifter rust test simulates typical city driving conditions, and is carried out in a six cylinder Chevrolet Powerglide engine, operating at 2500 r.p.m. and a load of 45 B.H.P., with an oil temperature of 120° F. and a water temperature of 85-95° F. The test is run at these conditions for a total of forty hours, broken into five periods of four hours each, running time, with a four hour off period between runs. At the end of twenty hours, the dip stick, rocker arm shaft, and valve lifters are inspected for rust. Valve lifters free of rust are visually rated number 10 and badly rusted lifters are rated 1, with arbitrarily selected intermediate ratings.

A series of four runs was conducted to illustrate the marked superiority of the borated reaction product over the unborated product. The results are shown in the table below:

Modified Indiana rust test

Additive in SX Lubricating Oil	Test, Hours	Rust Rating		
		Dipstick	Rocker Arm	Valve Lifters
0.54% tallow amine-dimer acid-borate.	0	clean....	clean.....	10
	20	do.....	do.....	10
	40	do.....	very slight..	10
0.5% tallow amine (btms.)- dimer acid.	0	do.....	clean.....	8
	20	slight....	moderate....	10
0.55% tallow amine-VR-1 acid.	0	clean....	clean.....	8.5
	20	slight....	severe.....	10
	40	clean....	clean.....	10
None.....	20	severe....	severe.....	1 6.5

¹ Twelve lifters semi-stuck.

It will be observed from the above that tallow amine bottoms-dimer acid and tallow amine-Rohm & Haas VR-1 acid reaction product gave slight rusting of the dip stick, moderate to severe rusting of the rocker arm, and valve lifter ratings of 8 and 8.5 respectively. By contrast, at the end of the same 20 hour operating period, a borated tallow amine-dimer acid preserved the test engine in virtually unchanged condition, and after continuing the test for an additional twenty hours showed only very slight rusting of the rocker arm shaft, with still no rusting of the dip stick or valve lifters. These results are

also contrasted with a solvent-extracted (SX) lubricating oil without any anti-rust.

EXAMPLE IV

A lubricant oil containing 0.48% of the tallow amine-Hardesty acid-borate prepared in Example II above was tested under the conditions of the modified Indiana hydraulic valve lifter rust test, with results shown below. It will again be observed that rusting of the dip stick and valve lifters was entirely prevented, while only very slight rusting of the rocker arm shaft occurred. These results may be compared with the results shown in Example III using unborated amine-acid inhibitors.

Modified Indiana rust test

Additive in SX Lubricating Oil	Test, Hours	Rust Rating		
		Dipstick	Rocker Arm	Valve Lifters
0.48% tallow amine-Hardesty acid-borate.	0	clean....	clean.....	10
	20	do.....	very slight..	10

From the foregoing examples, it is evident that a borated reaction product of an N-alkyl alkylene polyamine with a polymeric long chain unsaturated polycarboxylic acid is a vastly improved rust inhibitor over the untreated reaction product at the same concentration level.

Rusting, of course, is not confined to internal combustion engines, and despite a common misconception, may occur whenever hydrocarbon oils are in contact with iron or steel surfaces. Refinery expenses amounting to millions of dollars annually are incurred in repairing and replacing processing equipment, tankage and product pipelines attacked by rusting. In the case of product pipelines and tankage, rusting is particularly severe since it is the common practice to employ different anti-rust additives in petroleum products of different compositions and/or boiling ranges, with each individual anti-rust being especially suited for only one certain type of product. Instances are known where a pipeline or tank alternatively carrying two or more petroleum products gives an unexpectedly short service life, a phenomenon evidently caused by an antagonism between two or more anti-rusts, each employed in a different product. In addition to this apparent antagonism, the storage of petroleum products in vessels wherein a water phase may be present, which is usually the case in storage tanks, gives rise to exceptional problems. If an anti-rust additive is to be employed, it must be capable of inhibiting rusting both in the oil phase and in the aqueous phase.

The additives of the instant invention are exceptionally suitable for incorporation in virtually all types of petroleum products, and satisfy the requirement of being able to prevent both oil-phase and water-phase rusting. To demonstrate this, several tests were made wherein a borated diamine-acid according to the present invention was incorporated into different refinery products, and the degree of rust inhibition measured and compared with rust inhibition provided by standard rust inhibitors.

These tests were carried out using the so-called bottle test. A sheet of 0.005 inch mild steel stock is abraded with #2 followed by #00 emery cloth and then with steel wool. Coupons 6" by 1/2" are cut from this sheet, wiped with a dry cloth, and immersed in one pint wide mouth bottles containing the test mixtures. These mixtures consist of 250 ml. of oil plus inhibitor solution, and 100 ml. of boiled distilled water. The bottles are covered with a Teflon sheet and a screw cap, rolled ten times horizontally to mix the contents, and allowed to stand upright for the required test. Thus, portions of the coupons are exposed to the aqueous, oil, and vapor phases. The amount of rust which appears on the coupons in the aqueous and oil phases is visually rated at appropriate times during the test period.

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EXAMPLE V

The utility of a borated tallow amine-Hardesty acid reaction product (Example II) was demonstrated as a rust inhibitor for commercial heater oils. Such oils are commonly used in home and light industrial applications, and have a boiling range between about 200 and about 700° F., usually between about 300 and 600° F. Frequently the initial boiling point is specified at between about 300 and 375° F., and the 95% distillation point may be between 500 and 650° F. Other specifications more or less generally applied to heater oils are an API gravity of not less than 40°, and a Tag closed cup flash of not less than 110° F. The following results were obtained in the bottle test.

Heater-oil bottle test

Additive in Heater Oil	2 days		7 days	
	oil	water	oil	water
0.002% tallow amine-Hardesty acid-borate.	clean.....	clean.....	clean.....	clean.....
None.....	5% rust.....	60% rust.....		

EXAMPLE VI

The inhibitor prepared in Example II was tested as an anti-rust in a gasoline suitable for internal combustion engines, and containing substantial amounts of sulfurous catalytically cracked components. Motor fuels generally boil between about 100 and 500° F., more commonly between about 150 and 400° F. The following results were obtained, at 0.001% and 0.002% concentrations, and are set out below along with results obtained with comparison tests of a commercial anti-rust.

Motor gasoline bottle test

Additive in Motor Gasoline	2 days		7 days	
	oil	water	oil	water
0.002% tallow amine-Hardesty acid-borate.	clean.....	clean.....	clean.....	75% slight rust.
0.001% tallow amine-Hardesty acid-borate.	do.....	do.....		
None.....	5% rust.....	80% rust.....		

EXAMPLE VII

Refinery fuel oil is a product primarily employed for local furnace firing. It is generally extremely corrosive, often containing as much as 5 wt. percent sulfur, as well as nitrogen, heavy metals, and chlorine compounds. Product specifications are rarely imposed on the oil, and heavy fuels may be said to have a boiling range anywhere from 200° F. to the final boiling point of the original crude oil. For captive use, heavy fuel oils may contain

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from 25 to 50% heavy catalytic cycle oil, the balance being vacuum distillation bottoms. The borated reaction product prepared in Example II was used in a concentration of 0.002%, and the following results were obtained.

Refinery fuel oil bottle test

Additive in Fuel Oil	2 days		7 days	
	oil	water	oil	water
0.002% tallow amine-Hardesty acid-borate.	clean.....	clean.....	1 spot.....	6 spots.....
None.....	30% rust.....	60% rust.....		

Hence it is apparent that a borated reaction product of an N-alkyl alkylene polyamine with a polymeric long chain unsaturated polybasic carboxylic acid is a vastly improved rust inhibitor over the untreated reaction product. When employed in small concentrations of from 0.0001 to 5% in engine lubricating oils, the additives of the instant invention remarkably reduce rusting of engine parts. Moreover, the novel additives of the invention are useful all-purpose rust inhibitors for addition to virtually all refinery product streams, and in concentrations of from 0.0001 to 5% therein are fully capable of imparting a high degree of rust inhibition to such varied products as motor gasoline and refinery residual fuels. An exceptional feature of the present additives is that they inhibit rusting of metals in contact with a water phase as well as in contact with an oil.

All percentages set forth in the specification and claim, unless otherwise stated, are expressed on a weight percent basis.

Thus, having described the invention, what is claimed is:

A new composition of matter prepared by mixing polymerized linoleic acid with an amine having the general formula $RNHCH_2CH_2CH_2NH_2$, wherein R is an alkyl radical containing 12 to 18 carbon atoms, said amine being mixed with said acid in a mole ratio of from about 0.5 mole to about 1.5 moles of said amine per mole of said acid at a temperature of from about 100° F. to about 300° F., subsequently reacting the mixture with boric acid in a mole ratio of from about 0.8 mole to about 2.5 moles of said boric acid per mole of said amine, and recovering a product therefrom.

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