

UNITED STATES PATENT OFFICE

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LUBRICATING COMPOSITION CONTAINING
THE REACTION PRODUCT OF BIURET AND
ALIPHATIC ESTERS OF HYDROXY ACIDSDavid E. Adelson, Berkeley, and Robert G. Larsen,
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of DelawareNo Drawing. Application August 27, 1948,
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This invention relates to novel reaction products having properties of greatly improving and stabilizing lubricants. This invention also pertains to lubricants, such as mineral lubricating oils, synthetic lubricants of hydrocarbon or non-hydrocarbon origin, and the like, containing therein a multi-functional additive having detergent and anti-ringsticking properties, as well as acting as an inhibitor of oxidation and corrosion.

It is well known that various lubricants whether doped or undoped, tend to oxidize and to form corrosive bodies and sludge, when used in modern engines and machines operating under ordinary conditions or at high speeds, elevated temperatures, heavy loads and/or other adverse conditions. Some of the deterioration products of lubricants formed during their use are hard carbonaceous materials which adhere to metal surfaces and cause scratching and scuffing of movable metal parts and the sticking of valves and piston rings in engines. In addition, presently known lubricants are generally incapable of maintaining a continuous lubricating film between movable metal parts, resulting in gradual or rapid wearing away of metal parts. The damage thus caused required replacement of such parts or even the complete overhauling of engines and machines, resulting in expensive loss of production and time.

In the case of the highest quality non-corrosive, stable lubricating oils, which have been highly refined for specific uses, or synthetic lubricants developed for specific or special uses, it has been observed that such oils or lubricants are generally highly susceptible to oxidation and deterioration, becoming progressively more corrosive in engines and machines even under ordinary operating conditions.

To improve the lubricating properties of oils and synthetic lubricants it has become the practice to blend with various lubricants, one and in most cases more than one addition agent, which additives have the effect or property of inhibiting deterioration of lubricants and impart to them certain beneficial properties. Thus, additives have been specifically designed which have the property of inhibiting corrosion of alloyed bearings such as copper-lead, cadmium-silver and the like, developed for automotive, diesel and aircraft engines. Acidic oxidation or decomposition components formed in lubricants during use readily attack these bearings but are inhibited or prevented from doing this by the formation of a corrosion protective film formed

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on the bearing surface with the aid of the additive. Additives have also been developed which possess the property of modifying the carbonaceous materials formed, by deterioration of lubricants, on piston rods, rings and valves, and other metal parts in internal combustion engines, automotive and truck engines, aviation engines, high speed diesel engines and the like. Such additives serve a very important function because, by modifying this carbonaceous material so that it can be removed easily, the tendency of engine parts to become stuck is inhibited so that ringsticking, piston scuffing, scratching and wearing away of other engine parts and material reduction of engine efficiency, are prevented or materially inhibited.

Other additives have been developed for the purpose of acting as detergents in lubricants in order to assist in the removal of soot or sludge, varnish, lacquer formed from deterioration of the oil when subjected to high operating temperatures. Detergents due to their cleaning action prevent the build-up of these deleterious materials and assist in removing those formed. Anti-wear additives have the property of reducing friction of movable metal parts of the same or different metals. Due to the function exerted or property imparted by such additives on lubricants, wear caused by direct frictional contact of metals can be greatly reduced. Also, additives have been developed to withstand extreme pressures, disperse impurities, solubilize certain additives and the like.

The development of numerous additives has been due to the fact that most, if not all additives are capable of functioning in substantially only one specific manner. Very few lubricant additives have the ability of improving a lubricant in more than just one respect. Thus, a good anti-oxidant might not be able to inhibit lacquer and varnish formation on piston rods or act as a detergent or corrosion inhibitor. In many cases it is found that an additive possesses very good properties in one respect, but is the cause of harmful formations and therefore detrimental as an additive in another respect. Therefore, other additives are frequently required to obtain a good stable lubricant. The combination of additives in lubricants wherein each additive exerts its influence without interfering with the function of other additives is a difficult matter to attain. In most cases additives co-react or interfere with each other. To prevent this great care must be taken in selecting the additives, mixing them in specific proportions and contin-

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uously watching and replacing additives which have stopped functioning or have deteriorated.

It is an object of this invention to improve the lubricating properties of various lubricating bases by the addition thereto of a minor amount of a multi-functional material. Another object of this invention is to add to compounded or doped lubricants a multi-functional material whereby a synergistic effect is produced, resulting in a product of accentuated and improved properties. Another object of this invention is to add to oleaginous materials, mineral lubricating oils, synthetic lubricants and the like, a multi-functional material so as to inhibit oxidation and corrosion and prevent the formation of sludge, varnish and lacquer in said lubricants even under adverse operating conditions. Still another object of this invention is to use in lubricating compositions, a multi-functional material which prevents ringsticking as well as the sticking of other engine parts due to deterioration of the lubricant. Also it is an object of this invention to use in oleaginous materials, e. g. in lubricating compositions, a multi-functional material which inhibits wear, scuffing, scratching and other damage to engine parts. Furthermore, it is an object of this invention to provide novel multi-functional improving and enhancing additives for lubricating bases. Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention consists of features which will be hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain embodiments of the invention, these being illustrative of but a few variations in which the principle of the invention may be employed.

Broadly stated, this invention is directed to the use in lubricants of a reaction product obtained by reacting biuret with a hydroxy ester, including natural fats, oils and waxes and their derivatives and miscellaneous compounds which can be exemplified by: castor oil, sperm oil, cottonseed oil, vegetable and animal phosphatidic materials and the like, as well as fractions and derivatives thereof, as well as glycerol monoricinoleate, glycerol monooleate, sorbitan monooleate, methyl ricinoleate, n-butyl citrate, sec-butyl glycolate, triethyl citrate, ethyl hydroxy isobutyrate, dioleoyl tartarate, trioleyl citrate, glycol monopropionate, glycerol monostearate, diamyl tartrate, sorbitan monostearate, sorbitan monoricinoleate, erythritol monooleate, erythritol monostearate, mannitol monooleate, sulfurized sperm oil, sulfurized cottonseed oil, reaction product of sperm oil and sulfur chloride.

The preparation of the reaction product of this invention is generally carried out at an elevated temperature of above 100° C. and generally between about 110° C. and 250° C. and under pressure for a period of time until the reaction is completed. The reaction product can be extracted by use of a suitable solvent and the solvent thereafter evaporated. The temperature pressure and time of reaction depend upon the reactive materials taking part in the reaction and are so adjusted so as to obtain the maximum yields of the desired reaction product.

To more clearly illustrate the present invention, the following examples are presented. It is to be understood, however, that various modifications can be resorted to without departing from the spirit of this invention.

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EXAMPLE I

Approximately 1.5 moles of methyl ricinoleate and about 2.3 moles of biuret were admixed and heated in an oil bath for about 72 hours at from about 148° to 151° C. The system was maintained at a pressure of 3 to 11 mm. and the evolved gases were pulled through a sulfuric acid trap. At the end of the reaction period the reaction product was extracted with about two liters of hot toluene. The solvent is evaporated and the reaction product comprising (methyl ricinoleate)-allophanate, containing 4.6(8) % nitrogen remained as a viscous liquid which slowly crystallized to a soft oily solid.

EXAMPLE II

Approximately one mole of castor oil and about 3 moles of biuret were heated for about 96 hours at around about 155° to 160° C. and 11 to 18 mm. pressure in accordance with the procedure of Example I. After extraction by means of hot toluene, the resultant reaction product after the solvent was evaporated, contained 4.1(7) % nitrogen and appeared as a very viscous material which slowly gelled on standing.

EXAMPLE III

Approximately one mole of hydrogenated castor oil and about 6 moles of biuret were mixed and heated for about 158° to 165° C. and 13 to 22 mm. pressure in accordance with the procedure of Example I. After isolation by means of toluene extraction, the final product contained 3.6(6) % nitrogen.

EXAMPLE IV

Approximately 1 mole of sec.-butyl glycolate and about 1.5 moles of biuret were reacted for about 75 hours at a temperature of 110° to 120° C. and at 100 to 145 mm. pressure. The reaction product was isolated by methyl ethyl ketone extraction and contained about 17.7 % nitrogen.

EXAMPLE V

About 1.3 moles of n-butyl citrate and about 2 moles of biuret were stirred and heated for 72 hours at between about 145° and 150° C. and 5 to 16 mm. pressure. After isolation by means of toluene extraction the product appeared as a viscous liquid containing about 4.5 % nitrogen. Other reaction products of this invention which can be used to improve lubricants are:

Reaction product of castor oil with thiobiuret
Reaction product of linoleic acid with thiobiuret
Reaction product of lard oil acids with thiobiuret
Reaction product of castor oil acids with thiobiuret
Reaction product of ricinoleic acid with diethyl acetyl biuret
Reaction product of licanic acid with diethyl acetyl biuret
Reaction product of tartaric acid with diethyl acetyl biuret
Reaction product of citric acid with diethyl acetyl biuret
Reaction product of rapeseed oil with biuret
Reaction product of glycerol monooleate with biuret

Reaction products of this invention may be sulfurized, sulfo-phosphorized, phosphonized, halogenated, etc., with such reagents as, sulfur, sulfur halides, inorganic polysulfides, phosphorus sulfides, phosphorus, etc.

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EXAMPLE VI

Sulfurization of reaction products, as formed in Example I was accomplished as follows: About 76 gms. of reaction products as obtained in Example I was reacted with about 6.34 gms. of flowers of sulfur at 128° to 139° C. with constant stirring for about 16 hours. The sulfurized product was extracted with methyl ethyl ketone and the solvent evaporated leaving behind a viscous mass containing 4.2(3) nitrogen and 7.1(5) % sulfur.

EXAMPLE VII

Approximately 83 gms. of reaction products of Example II and about 7 gms. of sulfur were reacted for 17 hours at 110° to 131° C. The sulfurized product was isolated by means of toluene to yield a viscous product containing 7.6(2) % sulfur and 3.4(4) % nitrogen.

Base lubricants which may be improved by addition of minor amounts of reaction products of this invention may be selected from a wide variety of natural oils such as mineral oil, vegetable, animal or marine oils and/or their mixtures. In addition, synthetic lubricants may be used such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides; organic esters, e. g. 2-ethyl hexyl sebacate, dioctyl phthalate, trioctyl phosphate, polymeric tetrahydrofuran, polyalkyl silicone polymers, e. g. dimethyl silicone polymers and its halogenated derivatives, etc. Mixtures of natural and synthetic lubricants can be used.

To illustrate the pronounced improvement obtained in lubricating compositions by the addition of reaction products of this invention the following data is given:

Compositions of this invention were evaluated as extreme pressure agents by use of the Four-ball extreme pressure lubricating tester similar in principle to the Boerlage apparatus described in the magazine, Engineering, volume 136, July 14, 1933. This apparatus comprises four steel balls arranged in pyramid formation. The top ball is rotated by spindles against the three bottom balls which are clamped in a stationary ball holder. The balls are immersed in the composition to be tested. Tests were run for two hours at 700 R. P. M. under 7 kg. load and at a control temperature of 130° C. The diameter of the wear scars worn on the three balls from the base of the pyramid were measured, and the average taken as the true indication of wear.

Table I

WEAR EVALUATION IN THE MULTIPLE FOUR-BALL MACHINE AN SAE 20 WESTERN LUBRICATING OIL EMPLOYED

Additive	Amount Percent Weight	Scar diameter (mm.) at 7 kg. load
None	0	0.70
Reaction product of Ex. I	1	0.22
Reaction product of Ex. II	1	0.26
Reaction product of Ex. III	1	0.33
Reaction product of Ex. IV	1	0.23
Reaction product of Ex. V	1	0.27
Reaction product of Ex. VI	1	0.31

Doped and undoped oils were tested by a test known as the Thrust Bearing Corrosion Test (described in the National Petroleum News, September 17, 1941, pp. R-294-296) which is carried out as follows: A hardened steel disc is made to rotate for 20 hours under constant pressure against three flat copper-lead bearings. The

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bearings assembly rests in a steel cup filled with the oil to be tested and the temperature of the oil is maintained at a predetermined figure by thermostatic control. The bearings are weighed before and after the test; the difference in weight representing the loss sustained during the test.

Table II

TESTS IN THRUST BEARING CORROSION MACHINE
FIXED CONDITIONS: CU-PB BEARINGS, 20 HOURS
DURATION 125 P. S. I., 2400 R. P. M., SAE 20 WESTERN LUBRICATING OIL WAS EMPLOYED

Additive	Amount Percent Weight	Loss per sq. cm. of bearing surface—				
		110° C ¹	120° C ¹	130° C ¹	140° C ¹	150° C ¹
Reaction product of Ex. VI	1.3	-----	² 0.52	² 5.0	² 1.4	² 11.8
Reaction product of Ex. VII	1.4	0.12	-----	0.2	8.0	-----
None	-----	0.1	24.3	28.1	76.9	74.5

¹ Temperature.

² Loss.

Compositions of this invention were also subjected to the Shell Automatic Oxidation Stability Test under the conditions denoted below in order to determine the stabilizing effect reaction products of this invention have on base oils. The results were as follows:

Table III

Base Oil	Additive	Amount Percent Weight	Catalyst	1800 ml. O ₂ Time in Hours
White Oil	Reaction product of Ex. VI	1.4	-----	1.6
Do	Reaction product of Ex. VII	1.3	-----	76.4
Do	Reaction product of Ex. VI	1.4	0.5% crank-case catalyst	17.7
120 Grade AVI Aviation Oil	Reaction product of Ex. VI	1.4	-----	80
Do	Reaction product of Ex. VII	1.3	do	120

In addition to the above properties the addition of reaction products of this invention to mineral lubricating oils inhibits lacquer formation in engines operating under the most adverse conditions. Also reaction products of this invention can be used as valuable constituents of heavy duty oils, motor oils, diesel oils, aviation oils, turbine oils, synthetic oils and the like, because of their anti-corrosion, anti-oxidation and anti-wear properties. Besides their utility as lubricating oil additives, reaction products of this invention are useful as anti-oxidants for natural and synthetic rubber and other organic materials which are subject to oxidation deterioration. The amount of additive used can be varied over wide limits, but generally it is not necessary to use more than 5% by weight of the reaction product although amounts of as high as 10% can be used, but preferably only between about 0.1 to 2.0% by weight is added to base lubricants.

Because of its synergistic effect the reaction product of this invention can be combined with other additives in lubricants, such as, blooming agents, pour point depressants or viscosity improvers, extreme pressure agents, anti-foaming agents and the like. Among the specific additives which can be used are oil-soluble detergents which include metal as well as organic bases. Metallic bases include those of the alkali metals,

Cu, Mg, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

Examples of detergent forming acids are the various fatty acids of say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax) chlorinated fatty acids, rosin acids, aromatic carboxylic acids including fatty acids, aromatic hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid monoesters, aromatic keto acids, aromatic ether acids, diphenols as di-(alkylphenol) sulfides and disulfides, methylene bis alkylphenols; sulfonic acids such as may be produced by treatment of alkyl aryl hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid monoesters; phosphoric, arsonic and antimony acid mono and diesters, including the corresponding thiophosphoric, arsonic and antimony acids; phosphonic and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate diester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides.

Non-metallic detergents include compounds such as the phosphatides such as lecithin and cephalin, certain fatty oils as rapeseed oils, volatized fatty or mineral oils and the like.

An excellent metallic detergent for the present purpose is the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also alkaline metal salts of alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Anti-oxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, penta-methyl-phenol, 2,4-dimethyl-6-tertiary-butyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-ditertiary-butyl-4-methyl phenol, 2,4,6-tritertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenylamine, phenyl-beta-naphthylamine, phenyl-alpha-naphthylamine, dinaphthylamine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; alkali metal and alkaline earth salts of sulfonic acids and fatty acids; organic compounds containing an acidic radical in close proximity to a nitrile, nitro or nitroso group (e. g. alpha cyano stearic acid).

Extreme pressure agents which may be used comprise: esters or phosphorus acids such as triaryl, alkyl hydroxy aryl, or aralkyl phosphates, thiophosphates or phosphites and the like; neutral aromatic sulfur compounds or relatively high boiling compounds such as diaryl sulfides, diaryl disulfides, alkyl aryl disulfides, e. g. diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and tri-sulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc., in which the sulfur is strongly bonded; sulfurized long chain olefins such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons, such as chlo-

rinated paraffin, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc.; or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds. Depending upon the additive used and conditions under which it is used, the amount of additive used may vary from 0.01 to 2% or higher. However, substantial improvement is obtained by using amounts ranging from 0.1 to 0.5% in combination with phosphorus sulfide-unsaturated cyclic ketone reaction products of this invention.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

We claim as our invention:

1. A lubricating composition comprising a major amount of a lubricating oil and a minor amount sufficient to inhibit wear and oxidation of a reaction product of a biuret and aliphatic esters of hydroxy acids, said reaction product being formed by heating the reactants in the ratio of about 1:1 to 6:1 mols, respectively, and at a temperature between 100 and 250° C. for a period of 30-100 hours.

2. A lubricating composition comprising a major amount of a lubricating oil and a minor amount sufficient to inhibit wear and oxidation of a reaction product of a biuret and an aliphatic ester of a hydroxy acid, said reaction product being formed by the reactants in the mol ratio of 1:1 to 6:1 mols, respectively, at a temperature between 100 and 250° C. for a period of 20-100 hours, and retreating said reaction product with a sulfurizing agent at a temperature of at least 110° C. for a period of at least 16 hours.

3. A lubricating composition comprising a major amount of a mineral lubricating oil and from 0.1 to 10% by weight of a reaction product of a biuret and an aliphatic ester of a hydroxy acid, said product having been formed by heating the reactants in the ratio of about 1:1 to 6:1 mols, respectively, and at a temperature between 100 and 250° C. for a period of 30-100 hours.

4. A lubricating composition comprising a major amount of a lubricating oil and from 0.1 to 10% by weight of a reaction product of biuret and an aliphatic ester of a hydroxy acid, said product having been formed by heating the reactants in the ratio of about 1:1 to 6:1 mols, respectively, and at a temperature between 100 and 250° C. for a period of 30-100 hours.

5. A lubricating composition comprising a major amount of a mineral lubricating oil and from 0.1 to 10% by weight of a reaction product of biuret and a hydroxy fatty acid glyceride, said reaction product having been formed by heating the reactants in the ratio of about 1:1 to 6:1 mols, respectively, and at a temperature between 100 and 250° C. for 30-100 hours.

6. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount sufficient to inhibit wear and oxidation of a reaction product of castor oil with biuret in the ratio of about 1 to 3 mols, respectively, and at a temperature above 155° C., said

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reaction being carried out in the absence of the oil base, and retreating said reaction product with sulfur at a temperature of at least 110° C. and for a period of at least 16 hours.

7. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount sufficient to inhibit wear and oxidation of a reaction product of methyl ricinoleate with biuret in the ratio of about 1.5 to 2.3 mols, respectively, and at a temperature above 148° C., said reaction being carried out in the absence of the oil base, and retreating said reaction product with sulfur at a temperature of at least 110° C. and for a period of at least 16 hours.

8. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount of from 0.1 to 10% of a reaction product of castor oil with biuret in the ratio of about 1 to 3 mols, respectively, and at a temperature above 155° C., said reaction being carried out in the absence of the oil base.

9. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount of from 0.1 to 10% of a reaction product of methyl ricinoleate with biuret in the ratio of about 1.5 to 2.3 mols, respectively, and at a temperature above 148° C., said reaction being carried out in the absence of the oil base.

10. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit wear and oxidation, of a reaction product of biuret and

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castor oil, said reaction product being formed by reaction of the reactants in the mol ratio of 1:1 to 6:1 respectively, at a temperature between 100 and 250° for a period of 20-100 hours and retreating said reaction product with sulfur at a temperature of at least 110° C. for a period of at least 16 hours.

11. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit wear and oxidation, of a reaction product of biuret and methyl ricinoleate, said reaction product being formed by reaction of the reactants in the mol ratio of 1:1 to 6:1 respectively, at a temperature between 100 and 250° C. for a period of 20-100 hours and retreating said reaction product with sulfur at a temperature of at least 110° C. for a period of at least 16 hours.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,066,173	Calcott et al. -----	Dec. 29, 1936
2,316,903	Van Ess -----	Apr. 20, 1943
2,339,796	Musher -----	Jan. 25, 1944
2,352,669	Van Ess -----	July 4, 1944
2,377,909	Van Ess -----	June 12, 1945
2,408,090	Musher -----	Sept. 24, 1946