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3,220,949

LUBRICATING OIL COMPOSITIONS CONTAINING IODINE AND ASHLESS NITROGEN-CONTAINING OIL-SOLUBLE DERIVATIVES OF ALKENYL SUCCINIC ANHYDRIDE

Charles E. Bell, Jr., Norfolk, Va., and Philip Zaybekian, Parsippany-Troy Hills, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware
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3 Claims. (Cl. 252—51.5)

This invention relates to lubricating compositions containing iodine and ashless nitrogen-containing oil-soluble derivatives of alkenyl succinic anhydrides, which compositions exhibit extremely low coefficients of friction without being excessively corrosive to metals. It additionally relates to a method of reducing the metal corrosivity of iodine-containing lubricating compositions.

It has recently been discovered that iodine, in very small quantities, acts as an exceptionally effective oiliness agent in lubricating compositions to thereby considerably reduce the coefficient of friction between relatively moving surfaces. For example, copending application S.N. 170,249 discloses that as little as 0.0001 wt. percent of iodine, dispersed in a suitable carrier medium such as lubricating oil, drastically lowers the coefficient of friction existing between two rubbing surfaces contacted by the carrier medium. For example, 0.00375 wt. percent of iodine in a mineral oil carrier medium is able to lower the coefficient of friction more than 50%. It is additionally disclosed in the aforesaid application that the exposure of metal rubbing surfaces to iodine results in a beneficial carryover effect; i.e., the low frictional effect lasts for a significant period subsequent to the removal of the surfaces from contact with iodine. Additionally, it has been specifically found that the reduced coefficient of friction induced by the presence of 0.75 wt. percent iodine enabled approximately a 12% reduction in the frictional horsepower of a Chevrolet V-8 engine, as well as a 5% reduction in fuel consumption as compared with a conventional motor oil.

As a further example, copending application S.N. 204,043 discloses the same beneficial effect of iodine in lubricating compositions, with the added feature that the iodine may be embodied in various conventional polymeric lubricating additives as distinguished from the use of elemental iodine per se. Thus, for example, the use of an iodine-treated phosphosulfurized polybutene in a suitable base oil exhibited greater than a 50% reduction in friction as compared to the same base oil with a like amount of the untreated phosphosulfurized polybutene.

While it can be seen from the above that the inclusion of iodine, either in its elemental state or combined with conventional lubricating additives, is highly beneficial in reducing the coefficient of friction between metallic rubbing surfaces to thereby enable the fuel consumption of an engine to be appreciably reduced, a major drawback has sometimes been experienced; namely, that the beneficial effect of the iodine is offset by the occurrence of excessive corrosion of the metallic surfaces in contact with the iodine-containing oil compositions. This corrosion naturally limits the usefulness of iodine-containing lubricating oil compositions in certain applications, particularly in the lubrication of valve train assemblies wherein the tappets and cams become heavily rusted. The excessive rust in turn leads to wear of the rusting parts, as the particles of rust are gradually dislodged from the metallic surface.

It may be seen, therefore, that a considerable advance in the lubricating application field would be achieved by the discovery of suitable iodine-containing lubricating oil compositions which exhibit reduced corrosivity as com-

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pared to the compositions heretofore known. It has accordingly been discovered, and forms the basis of the present invention, that the inclusion of ashless nitrogen-containing oil-soluble derivatives of alkenyl succinic anhydrides effectively reduces the corrosive effects of iodine on metallic surfaces. By inclusion of such derivatives, the aforementioned compositions disclosed in copending applications S.N. 170,249 and 204,043 can be significantly improved in respect to their corrosiveness towards metals. Accordingly, for purposes of complete disclosure, copending applications S.N. 170,249 and S.N. 204,043 are hereby incorporated by reference. However, certain portions of those applications will be set forth in the present application where necessary for a complete understanding of the present invention.

The concentration of iodine in the compositions of the present invention will depend upon whether the iodine is used in its elemental state or whether it is contained in polymeric additives such as those described in S.N. 204,043. For the utilization of elemental iodine, the compositions of the invention will generally comprise a major proportion of a suitable lubricating oil; 0.0001 to 0.99, preferably 0.001 to 0.90, wt. percent iodine and a corrosion-inhibiting amount, e.g. about 0.01 to 10 wt. percent, preferably 0.5 to 5 wt. percent, of the alkenyl succinic anhydride ashless nitrogen derivative. Where the iodine is contained in polymeric additives such as those disclosed in S.N. 204,043, the amount of iodine contained in such additives will generally be about 10 to 90 wt. percent, preferably 20 to 80%, and most preferably 40 to 80%, based on the weight of the polymeric additive. Lower iodine concentrations may also be used. The final lubricating compositions in this case will generally contain a major amount of lubricating oil, a total iodine concentration of about 0.005 to 3.0 wt. percent, preferably 0.01 to 0.8 wt. percent, and a corrosion-inhibiting amount of the alkenyl succinic anhydride derivative, e.g., about 0.01 to 10 wt. percent, preferably 0.5 to 5 wt. percent.

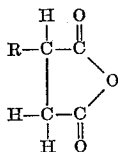
Suitable lubricating oils include the neutral lubricating oils having viscosities between 50 SUS and 2000 SUS at 100° F. or bright stocks having viscosities between 90 and 300 SUS at 210° F. The term "lubricating oil" is not intended to be limited to any specific application but of course may include cutting oils, metal working oils, pneumatic equipment oils, spindle oils, gear oils, motor oils, etc. Additionally, the lubricating oils contemplated include the straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes or, if desired, various blended oils can also be employed. Additionally, various synthetic lubricating oils made from esters, polysiloxanes, carbonates, formals, polyglycols, and the like may also be utilized.

As mentioned above, the iodine can be utilized in its elemental state or can be contained in various polymeric lubricating oil additives. Such iodine-containing polymeric additives are fully described in copending application S.N. 204,043, and include the oil-soluble homopolymers and copolymers formed from C₂ to C₃₀ olefins C₄ to C₃₀ ethylenically mono-unsaturated esters. The molecular weight (Staudinger) of these polymers will usually be within the range of 300 to 500,000, e.g., 500 to 60,000. Specific examples of such polymers utilized in the examples of S.N. 204,043 are: polybutene; phosphosulfurized polybutene; and ethoxylated, hydrolyzed, phosphosulfurized polybutene; wherein the polybutene has a molecular weight of about 780.

The ashless nitrogen-containing derivatives of alkenyl succinic anhydrides are generally prepared by reacting an alkenyl succinic anhydride with a basic nitrogen-containing material to thereby convert the acid groups of

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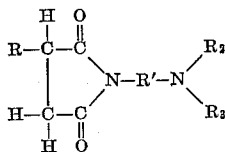
the anhydride to the corresponding derivative. The alkenyl succinic anhydride is first prepared by reacting maleic anhydride with an organic compound having a double bond at one end, e.g., a poly- α -olefin, to thereby produce an intermediate compound having the formula:



wherein R is an alkenyl radical, either substituted (e.g., chlorinated or sulfurized) or unsubstituted. R should be of sufficient size to impart oil solubility to the final product and will usually contain a total of 40 to 250, preferably 70 to 120 carbon atoms. Because of its readily availability and low cost, R is preferably a polymer of a C_2 to C_5 mono-olefin, having a molecular weight of about 400 to 3000, e.g. about 700 to 2500. Examples of such mono-olefins are ethylene, propylene, 1-butene, etc., with a particularly preferred mono-olefin being isobutylene. A preferred intermediate compound is polyisobutenyl succinic anhydride which is formed by the reaction between maleic anhydride and polyisobutylene.

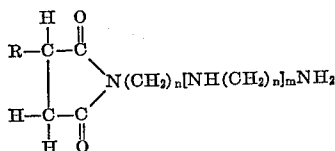
The preparation of the above-described alkenyl succinic anhydride has been disclosed, for example, in U.S. 3,018,250, column 3 lines 57-71, Example I.

The resulting intermediate compound is then reacted with any of a variety of nitrogen-containing compounds to form the ashless derivatives contemplated for use in the present invention. For example, the intermediate compound may be reacted with a dialkylaminoalkylamine as taught, for example, by U.S. 3,018,250. Suitable reactants of this type include dimethylaminomethylamine, dimethylaminopropylamine, methylpropylaminoamylamine, etc. In this instance, the final condensation product may be typified by the formula:



wherein R is as defined previously; R' is an alkylene radical, e.g., ethylene, propylene, butylene radicals; and R_2 and R_3 are C_1 to C_5 alkyl radicals. Where R is the preferred polyolefin, i.e. polyisobutylene, the above product will be an N-dialkylaminoalkyl monoalkenyl succinimide, e.g., N-dialkylaminoalkyl polyisobutenyl succinimide.

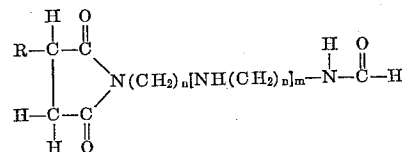
Additionally, the intermediate compound may be condensed with an alkylene polyamine such as ethylene diamine, diethylene triamine, tetraethylene pentamine, octaethylene nonamine, propylene diamine, tetrapropylene pentamine, etc. The reaction with tetraethylene pentamine is particularly disclosed in Australian patent application 63,803. A simple reaction procedure involves heating the two materials together while removing the water of condensation. The final condensation product may be typified by the formula:



wherein R is as defined previously, n is a number of 1 to 5, and m is from 0 to 10. This type of product may be used as is or may be further modified by various recently discovered procedures. For example, one such procedure

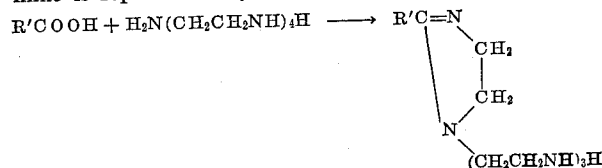
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involves reacting the above condensation product with formic acid to convert at least one of the amine groups to a formamide group. This reaction is carried out with the removal of 1 molecule of water for every molecule of formic acid reacted, and is readily accomplished by refluxing the reactants preferably with a solvent present as an entraining agent. A typical product resulting from such reaction with formic acid may be represented by the following general formula:

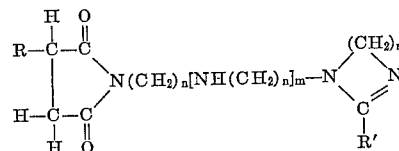


wherein m and n have the meanings given above and the terminal amine group has been converted to a formamide. The above product is formed when 1 mole of formic acid is used per mole of the succinimide. Where an excess of formic acid is used, e.g., 2 moles of formic acid per mole of succinimide, then the resulting product will be characterized by the presence of formamide groups along the length of the polyamine chain.

A further variation of the N-substituted alkenyl succinic anhydride type of additive which is suitable for use in the present invention is a condensation product of the above-described alkenyl succinic anhydride and an imidazoline. The imidazoline is first prepared by a condensation reaction of a monocarboxylic acid with a polyamine. The reaction may be typified as follows, wherein the polyamine is represented by tetraethylene pentamine:



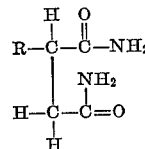
Examples of suitable carboxylic acids for use in the above reaction include acetic acid, capric acid, oleic acid, stearic acid, etc. Suitable polyamines include ethylene diamine, propylene diamine, tetrapropylene diamine, etc. The reaction is carried out by simple mixing of substantially equal molar proportions of the acid and amine, followed by heating to reflux and removal of the water of condensation. The resulting imidazoline is then reacted with the alkenyl succinic anhydride to produce a final product having the general formula:



wherein R and m and n have the meanings previously mentioned, and R' is a C_1 to C_{20} hydrocarbon, e.g., alkyl radical.

Also contemplated for use in the present invention are various nitrogen derivatives of alkenyl succinic anhydride wherein the carboxy groups are modified with nitrogen-containing materials. Examples of such derivatives include the following:

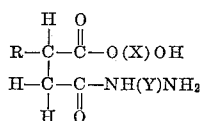
(1) Diamides having the general formula:



wherein R is as defined previously; the diamide being formed by the reaction of the alkenyl succinic anhydride with urea.

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(2) Compounds having the formula:



formed by esterifying one carboxy group of alkenyl succinic anhydride with a polyglycol, and amidating the other carboxy group with a polyamine, wherein X and Y in the above formula represent the center of the glycol and the polyamine, respectively, and R is as previously defined.

It is to be understood that still further variations of N-substituted alkenyl succinic anhydride are contemplated for use in the present invention, and that the scope of the invention is not limited to the specific derivatives described above.

Various other conventional lubricating additives may of course be included in the compositions of the present invention. These other agents include dyes, pour depressants, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, thickeners, viscosity index improvers, resins, rubber, other polymers, colloidal solids, soaps, sludge dispersants, and antioxidants. Numerous other agents will be obvious to those skilled in the art.

The compositions of the invention are readily prepared by simple admixture of the various ingredients. Concentrates of these compositions can also be prepared.

The following is a direct quotation from Example 1 of copending application S.N. 170,249, and is an illustration of the utility of iodine-containing lubricating compositions.

EXAMPLE OF S.N. 170,249

"In order to evaluate the compositions of the examples, they were tested in a rotating cylinder apparatus designed to measure metallic contact and friction between sliding, lubricated surfaces. Other noninventive compositions were also evaluated for comparison purposes. A complete description of this apparatus was given in a paper entitled, "Metallic Contact and Friction between Sliding Surfaces," by M. J. Furey, presented at the 1960 Joint ASLE-ASME Lubrication Conference, October 19, 1960, in Boston, Mass. This paper has been published by the American Society of Lubrication Engineers, 5 N. Wabash Ave., Chicago 2, Illinois, under the above-noted title in ASLE Transactions, volume 4, Number 1, pages 1-11, April 1961. The apparatus has also been described in copending application S.N. 80,474 filed January 3, 1961 by M. J. Furey and J. A. Wilson. The paper and copending application are herewith incorporated in their entirety in this application.

"The apparatus consists basically of a fixed metal ball loaded against a rotating steel cylinder. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between the two surfaces. It is expressed as the percent of the time that metallic contact occurs in a given period of time. Friction between the ball and cylinder is recorded simultaneously with contact. This is noted as coefficient of friction which is the ratio of friction force to the load. It has been found that there is, in general, a good correlation between metallic contact measured in this manner and the amount of surface damage which occurs.

"The evaluations of the compositions were obtained under the following conditions unless otherwise noted:

"System: AISI 52100 steel 1/2" diam. ball on 1 3/4" diam. cylinder

Load: 240 grams (54,700 p.s.i. mean Hertz pressure)

Speed: 240 r.p.m. (56 cm./sec. sliding velocity)

Time: 32 minutes

Temperature: 77° F.

"A solution containing 0.7 wt. percent iodine was prepared by adding elemental iodine to a solvent-extracted,

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paraffinic, neutral mineral oil having a viscosity of 100 SUS at 100° F. and mixing at ambient temperature. The resultant blend was clear with a dark amber color. A portion of this blend was set aside and the remainder diluted to give a blend having a 0.075 wt. percent concentration of iodine. The latter blend was further diluted in the same manner and treated identically as the first blend. This procedure was carried out until there were five blends containing the concentrations of 0.75 wt. percent, 0.075 wt. percent, 0.0075 wt. percent, 0.00375 wt. percent, and 0.00075 wt. percent iodine. The iodine blends and the mineral oil base alone with no additives were evaluated in the ball-on-cylinder device. The evaluation was in terms of percent metallic contact and coefficient of friction. The blends were labeled from A through F. The average results of several evaluations and the designations of particular blends are given in Table 1 following.

TABLE 1.—EFFECT OF IODINE ON METALLIC CONTACT AND FRICTION
[Base oil: Mineral oil (100 SUS @ 100° F.). Time: 32 minutes]

Blend	Concentration of Iodine (Wt. Percent)	Average Percent Metallic Contact	Average Coefficient of Friction
A	0.75	85	0.090
B	0.00075	89	0.090
C	0.00375	65	0.040
D	0.0075	13	0.005
E	0.075	1	0.005
F	0.75	1	0.020

"As can be seen by the above data from Table 1, the iodine has a pronounced effect in reducing friction and metallic contact. Even more remarkably, the effect occurs at a concentration of iodine as little as 0.00375 wt. percent. At 0.0075 wt. percent iodine concentration, there is a significant reduction in metallic contact and a more than 50% reduction in friction.

"These effects are unusually large. For example, the average reduction in friction for blends containing 0.0075% iodine or more was 89%. The average reduction in metallic contact for the same oils was about 94%."

The present invention may be further understood by reference to the following examples, which are given for illustrative purposes only and are not to be construed as limiting the scope of the present invention.

Example 1

Two lubricating oil compositions were prepared containing elemental iodine and tested by a Volkswagen Valve Train Wear Test. This test is a cyclic valve train wear test which is run using a 4-cylinder Volkswagen engine equipped with premeasured cams and tappets. At the end of the test, the valve train is disassembled and the cams and tappets are measured. The test is considered a "fail" if the wear on any cam or tappet exceeds 0.0010 inch. Each cycle of the test consists of the following: 5 minutes at 60 r.p.m. with no-load; 10 minutes at 1200 r.p.m. with no-load; 1 minute shutdown. These cycles are continued for a total test duration of 100 hours.

The significance of the above test with regard to the purposes of the present invention is that increased wear values on the tappets and came of the valve train assembly indicate excessive rusting of these parts and subsequent flaking-off of the rust particles.

Composition A was an oil solution containing 0.45 wt. percent iodine which was prepared by adding elemental iodine to a solvent extracted, paraffinic, neutral mineral oil having a viscosity of 100 SUS at 100° F. and mixing at ambient temperature. The composition also contained conventional lubricating additives calcium sulfonate and calcium-barium nonyl phenol sulfide in amounts of 0.2

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wt. percent and 0.5 wt. percent, respectively, on an active ingredient basis.

Composition B, a composition of the present invention, was similar to Composition A except that it contained 0.30 wt. percent elemental iodine and 2.4 wt. percent of "Oronite 1200" supplied by California Research Corp. The active ingredient in this material has been identified as the tetraethylene pentamine derivative of polybutenyl succinic anhydride wherein the polybutenyl group had a molecular weight of about 900. It was utilized as a 60 wt. percent active ingredient in oil. The composition also contained 6.6 wt. percent (40 wt. percent active ingredient) of a conventional V. I. improver comprising a terpolymer of mixed fumarates, vinyl acetate, and maleic anhydride.

Composition C was identical to Composition B except that the iodine was excluded.

The results of the Volkswagen Valve Train Wear Test are shown in the following table, which indicates the wear values for the various tappets and cams. In order for a tappet or cam to pass this test, a value no greater than 0.0010" must be obtained.

TABLE I.—VOLKSWAGEN VALVE-TRAIN WEAR TEST

Wt. Percent Ingredients	Composition		
	A	B	C
Iodine.....	0.45	0.30	0
"Oronite 1200" ¹	0	2.4	2.4
Wear:			
Tappets—			
Left:			
1.....	0.0016	0.0003	0
2.....	0.0021	0.0002	0
3.....	0.0023	0.0005	0.0003
4.....	0.0020	0.0002	0.0003
Right:			
1.....	0.0032	0.0003	0.0003
2.....	0.0040	0.0004	0.0002
3.....	0.0025	0.0016	0.0003
4.....	0.0086	0.0003	0.0003
Cams—			
1.....	0.0015	0.0001	0.0001
2.....	0.0028	0.0002	0.0001
3.....	0.0017	0.0001	0
4.....	0.0050	0.0002	0
Appearance of Tappets and Cams....	Heavily rusted	Negligible rust	No Rust

¹ 60 wt. percent active ingredient in oil.

As shown in the above table, Composition A containing 0.45 wt. percent iodine without inclusion of the alkenyl succinic anhydride derivative failed the Volkswagen test since not one tappet or cam met the passing value of 0.0010. Additionally, the tappets and cams were heavily rusted. Composition B, on the other hand, a composition of the present invention, which contained a lesser proportion of iodine but additionally contained the alkenyl succinic anhydride derivative, exhibited far superior results in the Volkswagen test. Thus, all tappets and cams passed the test except for right tappet #3. Also, a negligible amount of rust was noted on the tappets and the cams. For comparison purposes, Composition C, containing no iodine, easily passed the test.

It may be concluded from the above that nitrogen-containing derivatives of alkenyl succinic anhydrides are effective iodine corrosion inhibitors and provide a valuable means for enabling the beneficial use of iodine in lubricating oil compositions.

Example 2

The compositions shown below were subjected to a standard Shell Four-Ball Wear Test which was run for 2 hours at 150° C., 1800 r.p.m., and 10 kg. load. The staining balls were then observed, as recorded below. The oil and the "Oronite 1200" were the same as used in Example 1.

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TABLE II.—FOUR-BALL WEAR TEST

Composition:	Condition of balls
Oil+0.367% iodine	Red-brown stain.
Oil+0.434% iodine	Red-brown stain.
Oil + 0.521% iodine + 2.4% ¹	
"Oronite 1200"	No stain, balls clean.

¹ 60 wt. percent active ingredient.

The beneficial effect of the nitrogen-containing alkenyl succinic anhydride derivative is again observed, in the elimination of discoloration as shown in the above table.

Example 3

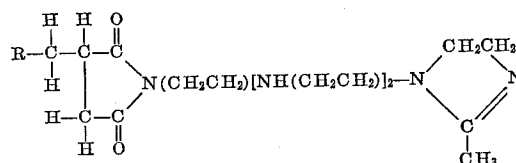
Example 1 is repeated exactly except that Composition B contains 0.55 wt percent of an iodine-containing polybutene in place of the elemental iodine, and the V.I. improver terpolymer is excluded. This iodine-containing polybutene is prepared as follows. One hundred grams of iodine crystals, 100 grams of polybutene having a Staudinger molecular weight of about 780 and 200 grams of diethyl ether as a solvent are mixed together to form a solution which is then allowed to stand at room temperature, i.e., about 75° F., for 24 hours. Next, the solution is filtered through filter paper to remove any excess iodine crystals. The filtrate is placed on a steam bath (about 160° F.) for about 3 hours to evaporate the ether. The final product (a dark viscous liquid) contains about 76 wt. percent iodine.

Example 4

Example 1 is repeated exactly except that the V.I. improver is excluded and the tetraethylene pentamine derivative of polybutenyl succinic anhydride, wherein the polybutenyl group has a molecular weight of about 1000, is utilized in place of the "Oronite 1200."

Example 5

Example 1 is repeated exactly except that the V.I. improver is excluded and 1.5 wt. percent (active ingredient) of an alkenyl succinic anhydride-imidazoline condensation product is used in place of the "Oronite 1200." This material may be typified by the structure:



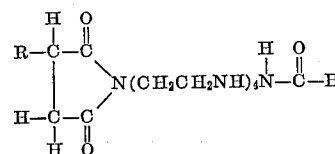
where R is a polyisobutenyl group of about 1000 molecular weight.

Example 6

Example 1 is repeated exactly except that the V.I. improver is excluded and 2.0 wt. percent of the diamide of polyisobutenyl succinic anhydride, wherein the polyisobutenyl group has a molecular weight of about 1000, is used in place of the "Oronite 1200."

Example 7

Example 1 is repeated exactly except that the V.I. improver is excluded and 0.5 wt. percent of a material having the structure



wherein R is a polyisobutenyl group having a molecular weight of about 1000, is used in place of the "Oronite 1200."

Example 8

Example 1 is repeated exactly except that the V.I. im-

prover is excluded and 3.0 wt. percent of N-diethylamino methylpolyisobutenyl succinimide, the polyisobutenyl group having a molecular weight of about 900, is used in place of the "Oronite 1200."

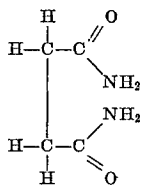
Example 9

Example 1 is repeated exactly except that the V.I. improver is excluded and 5.0 wt. percent of the reaction product obtained by reacting one mole of tetraethylene glycol and one mole of tetraethylene pentamine with two moles of polyisobutenyl succinic anhydride, the polyisobutenyl group having a molecular weight of about 900, is used in place of the "Oronite 1200."

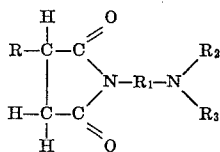
What is claimed is:

1. A lubricating composition comprising a major amount of lubricating oil, 0.0001 to 0.99 wt. percent iodine as a friction reducing agent, said composition having a tendency to corrode iron due to the presence of said iodine, and about 0.1 to 10 wt. percent of an oil-soluble ashless nitrogen containing derivative of alkenyl succinic anhydride containing a total of 40 to 250 carbon atoms in said alkenyl group, wherein said derivative has the ability to inhibit said tendency to corrode iron and is selected from the group consisting of:

(1) diamides of said alkenyl succinic anhydride, having the formula:

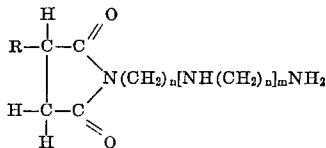


(2) dialkylaminoalkylamine derivatives having the formula:

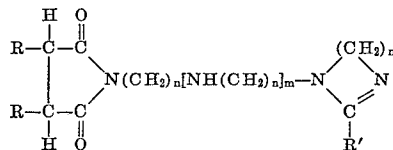


wherein R_1 is a C_2 to C_4 alkylene radical and R_2 and R_3 are C_1 to C_5 alkyl radicals;

(3) alkylene polyamine derivatives having the formula:



wherein n is 1 to 5 and m is 0 to 10; and
(4) imidazoline derivatives having the formula:

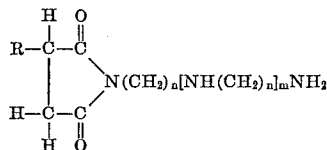


wherein n is 1 to 5, m is 0 to 10 and R' is a C_1 to C_{20} alkyl radical;

and wherein R in all of said formulas (1) to (4) is a C_{40} to C_{250} alkenyl group.

2. A lubricating oil composition comprising a major amount of mineral lubricating oil, a friction reducing amount of iodine within the range of about 0.001 to 0.90 wt. percent of elemental iodine and a rust corrosion inhibiting amount within the range of 0.1 to 10.0 wt. percent, of the alkenyl succinimide produced by reacting polyisobutylene succinic anhydride and tetraethylene pentamine, wherein said alkenyl group has a molecular weight of about 700 to 2500.

3. A lubricating oil composition comprising a major amount of mineral lubricating oil, about .001 to 0.90 wt. percent elemental iodine as a friction reducing agent, and a corrosion inhibiting amount, within the range of about 0.1 to 10.0 wt. percent of succinimide of the structure:



wherein R is a polyisobutenyl group of 700 to 2500 molecular weight, m is 0 to 10 and n is 1 to 5.

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DANIEL E. WYMAN, *Primary Examiner*.