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3,493,512

ALIPHATIC SECONDARY AMINE OXIDATION  
INHIBITORS

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No Drawing. Continuation-in-part of application Ser. No.  
409,291, Nov. 5, 1964. This application Feb. 27, 1967,  
Ser. No. 618,996

Int. Cl. C10m 3/26; C07c 87/123

U.S. Cl. 252—51.5

6 Claims

## ABSTRACT OF THE DISCLOSURE

An oxidation inhibitor for lubricants particularly syn-  
thetic ester lubricants comprising secondary amines hav-  
ing the following general structure:



wherein  $R_1$  and  $R_2$  are branched chain, saturated aliphatic  
hydrocarbon groups of from 15 to 24 carbon atoms, and  
are the hydrocarbyl or non-carboxyl portion of normally  
liquid, branched chain, saturated, aliphatic, monocarbox-  
ylic acids containing from 16 to 25 carbon atoms.

## BACKGROUND OF THE INVENTION

This invention is concerned with oxidation inhibitors  
for lubricant systems and more particularly with branched  
chain, saturated, aliphatic secondary diamines which are  
useful as oxidation inhibitors for synthetic ester lubricants.

Oxidation inhibitors are added to lubricant fluids to  
minimize oxidative decomposition of the fluid to acid  
products which tend to form sludge and to corrode the  
various metal surfaces with which the lubricant comes  
into contact. The demand imposed upon oxidation in-  
hibitors is closely related to the engine operating tempera-  
ture with an increase in engine temperature placing an in-  
creased demand upon the oxidation inhibitor. Thus, many  
oxidation inhibitors which give adequate protection at  
temperatures around the 300° F. level have substantially  
no utility at higher temperatures. With an increase in  
the sophistication of gas turbine engines has come an  
increase in the operating temperatures, the increase being  
from about 300° F. maximum temperature in the gas  
turbine engines utilized in aircraft propulsion in 1953  
to temperatures of 400–450° F. in modern gas turbine  
aircraft engines. At temperatures above 300° F., the con-  
ventional oxidation inhibitors, such as alkylated phenols  
and conventional petroleum lubricating oils fail to per-  
form their respective functions.

The secondary dialkylamine oxidation inhibitors of the  
present invention are capable of inhibiting oxidation of  
lubricant compositions at temperatures as high as 450°  
F. They have the further advantages that they are readily  
soluble in both hydrocarbon and synthetic lubricants and  
thus compatible with either type of lubricant system, they  
do not appreciably affect the liquidous characteristics of  
the base fluid, and they do not attack the rubber of elastom-  
er seals in turbine aircraft engines. One of the most  
difficult problems connected with the oxidation inhibitors  
heretofore developed which have been able to withstand  
high temperatures has been their tendency to attack the  
rubber or elastomer seals causing them to become hard  
and brittle and cease to perform. Some seals such as  
Viton-A, a fluorinated polymer, are depolymerized by  
many of the so-called high performance oxidation inhibi-  
tors.

In the past, probably the most popular oxidation in-

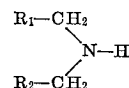
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hibitors for high temperature engine operations have been  
aromatic secondary amines such as p,p'-dioctyl-diphenyl-  
amine. While these aromatic secondary amines have been  
able to withstand high temperatures and have generally  
been stable antioxidants, they have suffered from the dis-  
advantage that they are "dirty," that is, they create a  
sludge which clogs filters and causes lubricant starvation  
when used at high temperatures, i.e. 450° F. One of the  
outstanding advantages of the branched aliphatic second-  
ary amines of the present invention is that they have out-  
standing cleanliness characteristics, enabling the engines  
to operate free from clogging caused by sludge accrual.

The aliphatic secondary amine oxidation inhibitors of  
this invention have, as noted earlier, excellent solubility  
characteristics and are miscible in all proportions with  
ester type lubricants, polyglycol lubricants and petroleum  
base oils without appreciably affecting the liquidous range  
of the base lubricants. They are also highly stable and are  
adapted to be employed with any of the conventional ad-  
ditives which are used in formulating a lubricant intended  
for high temperature service. Further, they remain liquid  
at extremely low temperatures, i.e. temperatures as low  
as -100° F., and thus they are useful in lubricants which  
must exhibit an extremely wide liquidous range. Some  
aliphatic secondary amines (dialkylamines), such as di-  
stearylamine, dimyristylamine, and dilaurylamine, have  
been used as oxidation inhibitors for petroleum lubricants  
in the past; however, they are generally unsatisfactory for  
use with ester lubricants because they are solids at room  
temperature and fall out of solution due to crystallization  
at low temperatures, i.e. temperatures below about -20°  
F. Furthermore, after having precipitated out at low tem-  
peratures, they are difficult to get back into solution and  
are frequently trapped by filters, resulting in clogging of  
the lubrication system.

## DESCRIPTION OF THE INVENTION

The oxidation inhibitors of this invention are secondary  
amines prepared from liquid branched chain higher fatty  
acids and have the general formula:



wherein  $R_1$  and  $R_2$  are both branched chain, saturated  
aliphatic hydrocarbon groups of from about 15 to 24  
carbon atoms, each group being in effect the hydrocarbyl  
or non-carboxyl portion or normally liquid, branched  
chain, saturated, aliphatic, monocarboxylic acids con-  
taining from about 16 to 25 carbon atoms. The branched  
chain monocarboxylic acids employed in the formation  
of the secondary amines of this invention are liquid at  
room temperature and are prepared by synthetic methods.  
An acid particularly suited for use in the preparation of  
the secondary amines which form the basis of this in-  
vention is one containing 18 carbon atoms formed as  
a by-product in the polymerization of naturally occur-  
ring unsaturated fatty acids in accordance with the method  
described in U.S. Patent 2,812,342 (hereinafter referred  
as the '342 patent and identified as isostearic acid).  
The '342 patent disclosure is incorporated herein by re-  
ference. According to the disclosure of the '342 patent,  
monounsaturated or polyunsaturated fatty acids are  
treated thermally in the presence of water with or with-  
out a catalyst to produce products which are known com-  
mercially as dimer acids. This process inherently pro-  
duces a substantial amount of by-product acids which are  
a mixture of monomeric acids. The monomer mixture,  
which is normally distilled in vacuo from the polymer-  
containing reaction product, includes saturated fatty acids  
which have not been affected by the polymerization treat-

ment, probably some unsaturated fatty acids which have not been affected by the polymerization treatment and fatty acids which have been structurally modified by the polymerization treatment in such a manner that they resist further polymerization.

Following the procedure outlined in the '342 patent, the monomeric fatty acids are hydrogenated to reduce the iodine value of the mixture to a level below 10 and perhaps as low as 3, thereby reducing any natural unsaturated fatty acids which may be present to saturated fatty acids. The hydrogenation treatment also reduces the iodine value of the fatty acids which have been structurally modified in some degree by the polymerization treatment. Further modifications may take place during the hydrogenation although it is not known to what extent structural modification of the acids takes place during that step. The resulting hydrogenated fatty acid mixture is then solvent separated to remove the normal solid fatty acids, such as stearic and palmitic acids. The remaining saturated fatty acid is a modified product which, while containing 18 carbon atoms, possesses a branched chain structure, a titre below 15° C. and an iodine value of substantially 3 to 10 and is referred to as isostearic acid. The exact structure of isostearic acid is not known; however, nuclear magnetic resonance tests have indicated that it is branched and has an average of at least 3 alkyl groups of 2 carbon atoms or more per molecule, indicating the presence of at least two side chains.

In manufacturing the isomeric C<sub>18</sub> acids for use in preparing the secondary amines of this invention, the process described in the '342 patent must be practiced very carefully to effect the best possible segregation of the different monomeric acids. For instance, if the hydrogenation process is practiced ineffectively, oleic acid will be present as an impurity in the end product and being unsaturated would be totally unacceptable as a component of an oxidation inhibitor. Further, if the solvent separation operation is not practiced effectively, stearic or other solid acids will be present and when converted to amines in accordance with the process of this invention and used as antioxidants will give the lubricant an unacceptably high pour point. In summary, the process of the '342 patent must be practiced with sufficient care that structurally modified acids are recovered without the presence of any objectionable quantity of undesirable impurities.

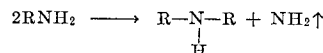
The '342 patent describes the branched chain C<sub>18</sub> fatty acids (isostearic acids) as structurally modified acids, (which they are in relation to the starting materials); however, these acids are more aptly described as structurally stabilized acids. The acids prepared by the method of the '342 patent receive two severe treatments, one a polymerization treatment which tends to both polymerize and to modify structurally the unsaturated acids, and the other a hydrogenation treatment which saturates and perhaps further modifies the structure of the acids. Hence, the structurally modified acids have become stabilized in the sense that they have been subjected to such rigorous treatment that they have developed their most stable structural form and thus are aptly described as "structurally stabilized."

The isostearic acid described above and in the '342 patent, forms, when converted into a secondary amine of this invention, the preferred embodiment of the invention.

Another normally liquid monocarboxylic acid which may be used in the preparation of the secondary amines of this invention is one which contains 22 carbon atoms and is prepared by the polymerization of isobutylene with oleic acid. The resulting product, on being hydrogenated to effect saturation, will consist essentially of a mixture of 9- and 10-secondary butylstearic acids. Still other liquid branched acids which may be used as 9-n-octylmargaric acid and 10-methylstearic acid. As

previously noted, the acids which may be used in the formation of the secondary amines of this invention should have from 16 to 25 carbon atoms. The secondary amine oxidation inhibitors derived from these acids must be fully compatible at use levels with the lubricant system and the lubricant must be liquid at a temperature of -65° F.

The secondary amines of the present invention may be prepared by reacting the saturated liquid aliphatic branched acids with ammonia to convert to the nitrile of the liquid branched acid use. The nitrile is recovered and hydrogenated to the amine form and the secondary amine is separated and used as the oxidation inhibitor of the present invention. One method for preparing the oxidation inhibitors of the present invention is as follows: The liquid branched aliphatic acid is heated to a temperature of from about 250° to about 350° C. (preferably 320°-330° C.) and ammonia is passed constantly into contact therewith with the water of reaction being removed. The reaction should be conducted at a pressure of from about 50 to 150 p.s.i. (preferably 90 to 100 p.s.i.) and should be continued until the reaction product is substantially a nitrile. After the nitrile has been recovered, it is hydrogenated using a standard hydrogenation catalyst such as nickel on keiselguhr, Raney nickel, palladium or platinum on suitable support, or other well known hydrogenation catalysts. The hydrogenation should be effected when using a nickel catalyst at pressures of from 50 to 400 p.s.i., preferably 300 to 400 p.s.i., and at temperatures of 150 to 250° C., preferably 200 to 225° C. During the hydrogenation process the nitrile is first converted to a primary amine and then in substantial part to a secondary amine as ammonia is split out. The reaction is as follows:



where R is the hydrocarbyl residue of the liquid branched aliphatic acid. After the nitrile has been substantially converted to the amine form, the amine product is cooled, filtered, and fractionated to separate the secondary amines from the primary amines and tertiary amines.

The secondary amine oxidation inhibitors of this invention may be used with a large number of lubricating oils, both mineral oils and synthetic oils including a wide variety of aliphatic, carboxylic acid esters which have been proposed for lubricant usage. Among these lubricants are the dialkyl (C<sub>6</sub>-C<sub>18</sub>) esters of aliphatic dicarboxylic acids (C<sub>6</sub>-C<sub>12</sub>), the principal diesters being those derived from adipic, azelaic, or sebacic acids and a C<sub>8</sub> to C<sub>10</sub> alcohol.

Specific examples of ester lubricants in which the oxidation inhibitors of this invention may be used are dioctylazelaate, di-2-ethylhexylsebacate, di-2-ethylhexyladipate, dilaurylazelaate, disecundaryamylsebacate, di-2-ethylhexylsuccinate, di-2-(2'-methoxyethoxy)ethylsebacate, di-2-(2'-ethylbutoxy)ethylsebacate, di-2-ethylhexylazelaate.

In addition to the aliphatic dicarboxylic acid esters described above, the secondary amine oxidation inhibitors of this invention may be used with polyester lubricants formed by the reaction of an aliphatic dicarboxylic acid, a glycol, and a monofunctional compound, which is either an aliphatic monohydroxy alcohol or an aliphatic monocarboxylic acid, in specified mole ratios. The instant oxidation inhibitors may also be used with complex esters formed by such reactions as that of a mixture containing specified amounts of 2-ethyl-1,3-hexanediol, sebacic acid and 2-ethylhexanol or by the reaction of a mixture containing adipic acid or azelaic acid, diethyleneglycol and 2-ethylhexanoic acid. Esters formed by reaction of a monocarboxylic acid and a glycol may also be used as the ester component. The acid component is usually an aliphatic acid containing at least 6 carbon atoms. The glycol component can be a straight glycol such as 1,6-hexanediol

but other glycols such as tetraethyleneglycol or dipropyleneglycol may also be used. Specific examples of the diesters of glycols are the following: di-n-decanoate of 1,4-butanediol, di-2-ethylhexanoate of 1,6-hexanediol, dilaurate of 1,4-hexanediol, and the dioctanoate of 1,5 pentandiol. Esters formed by reacting trimethylolalkanes (C<sub>2</sub>-C<sub>4</sub>) with various monobasic acids, primarily C<sub>5</sub>-C<sub>10</sub> acids, comprise another example of esters useful as the base fluid of lubricants which can be used with the compounds of this invention.

The secondary amine oxidation inhibitors of this invention are capable of withstanding the severe Pratt and Whitney 450° F. oxidation test. They out-perform at 450° F. p,p'-dioctyldiphenylamine, one of the most effective oxidation inhibitors heretofore developed for use in high performance (high temperature) engine operation.

The amount of secondary amine oxidation inhibitor to be employed in a given lubricant, will, of course, vary with the particular antioxidant chosen, the nature of the lubricant fluid, and the engine conditions to be encountered. Generally speaking, good results are obtained using amounts of from about 0.1-5.0% by weight of the secondary amine with the preferred range being from 0.5-2.0% by weight.

The oxidation inhibitors of this invention may be used with a number of other lubricant additives as well and in many instances it is preferred or necessary that additional materials be used. One additive which generally must be included is a metal deactivator such as PANA (phenyl-alpha-naphthyl-amine). Other conventional additives including rust inhibitors or materials which impart load carrying qualities, auxiliary oxidation inhibitors, if desired, and V.I. improvers may be used.

The present invention is further illustrated by the following examples which it should be understood are illustrative and not limitative of the scope of the invention.

#### EXAMPLE I

An oxidation inhibitor of this invention, diisostearylamine, was prepared in the following manner: sixty-five pounds of isostearic acid were charged into a 12 gallon autoclave equipped with stirrer. The acid was heated slowly to 320° C. under a constant flow of ammonia and with the use of a constant vent to remove the water of reaction. The pressure was maintained at about 90 to 100 p.s.i. After 7 hours the reaction products were analyzed and it was found that a considerable amount of the product was still in the amide form. The reaction was thus continued under the above-noted conditions for an additional 7 hours after which the product was almost exclusively isostearyl nitrile. The reaction was cooled and the product filtered through a No. 27 full-flow filter. Fifty-four pounds of isostearyl nitrile were recovered.

ples were taken to determine the neutralization equivalent values. When it had been determined that the product had been substantially hydrogenated to the amine form (3½ hours), the system was cooled to 150° C. The product, approximately 1000 grams, was blown from the autoclave and filtered using a filter aid (dicalite). The neutralization equivalent of the filtered product was 645. The filtered material was then topped at a pressure of 0.3 to 1.2 mm. of Hg and at a temperature up to about 260° C. to remove all of the primary amine. The residue 83.2% by weight was then given a distillation using a column of short length, under 0.3-0.4 mm. Hg pressure. The first fraction of the resulting product was removed at a pot temperature of 275-280° C. and a vapor temperature of 231° C. under a pressure of 0.3 ml. of mercury. This first fraction represented 1.3% by weight of the product and had a neutralization equivalent of 568. A second fraction which was diisostearylamine was then removed at a pot temperature of 280-300° C. and a vapor temperature of 258 to 270° C. under a pressure of 0.35 mm. of mercury. This fraction represented 72.2% by weight of the product prepared as described above, had a neutralization equivalent of 522, and was the fraction used as the oxidation inhibitor in the examples of this invention.

#### EXAMPLES II-V

Comparative oxidation tests were conducted upon a number of oxidation inhibitors, N-ethylaniline, bis(1, ethyl-3-methylpentyl)amine, p,p'-dioctyldiphenylamine, all commercially used amine oxidation inhibitors and diisostearylamine, an oxidation inhibitor of the present invention. The test procedure was as follows: 100 grams of a lubricant, trimethylolpropane dipelargonate monoheptanoate, containing an oxidation inhibitor in the amount indicated in Table I and a weighed copper coupon were placed in an Erlenmeyer flask. The flask was immersed in a silicone bath so that the surface of the sample was about one inch below the surface of the liquid bath.

An air tube was inserted into the flask and kept one inch above the surface of the sample. The air rate was adjusted to 16.8 cubic feet per hour. A 1 ml. sample was withdrawn by pipette periodically and analyzed. The contents of the pipette were drained through a 200 mesh screen and a 100° F. kinematic viscosity test was made using a 1 ml. Cannon Micro Viscometer (actual capacity is approximately 0.5 ml.). At the end of the test (after four days), the remainder of the sample was filtered through a 10 micron millipore filter. The copper coupons were weighed after being washed thoroughly with a solvent and weight loss was calculated as mg./cm.<sup>2</sup> of surface exposed. The results of the tests run upon the various amine oxidation inhibitors are shown below in Table I.

TABLE I

	Example			
	2	3	4	5
	1.5% N-ethyl-aniline, 0.5% PANA	1.0% dioctyl-diphenyl-amine, 1.0% PANA	2.5% bis(1-ethyl-3-methylpentyl)-amine, 0.5% PANA	2.5% diisostearylamine, 1.0% PANA
Viscosities cs. at 100° F.				
Original.....	20.1	22.1	19.4	21.7
1 day.....	24.8	24.5	25.7	23.5
2 days.....	35.9	26.9	36.8	25.4
3 days.....	50.0	30.3	51.3	28.8
4 days.....	72.3	35.8	77.1	33.2
Copper wt. loss, mg./cm. <sup>2</sup> .....	0.78	0.23	0.33	0.03

1000 grams of the isostearyl nitrile and 20 grams of 1% nickel catalyst, Harshaw Nickel 0104-P (50% active nickel on keiselguhr) were placed in a rocking autoclave. The system was vented with hydrogen to remove air and then pressurized to 300 p.s.i. with hydrogen. Heat was applied until the temperature reached 200° C. and the reaction was continued at this temperature and at a pressure ranging from 290-380 p.s.i. Intermediate sam-

As may be seen from the above test, the viscosity of diisostearylamine, the oxidation inhibitor of the present invention, was less affected over a period of time than any of the other amine oxidation inhibitors tested. N-ethylaniline and bis(1-ethyl-3-methylpentyl)amine show a viscosity rise far in excess of that which can be tolerated. It may also be noted that the copper corrosion was substantially less with diisostearylamine.

## EXAMPLES VI AND VII

In order to further compare the oxidation inhibiting properties of diisostearylamine and p,p'-dioctyldiphenylamine, both compositions were subjected to the Pratt and Whitney 450° F. oxidation test. The test was conducted in the following manner: 200 ml. of test solution comprising as the lubricant trimethylol propane dipelargonate, monoheptanoate, 1.0% by weight phenyl alpha naphthyl amine, a copper deactivator, and 2.5% by weight of oxidation inhibitor was prepared. One inch by one inch coupons of copper, steel, silver, titanium, magnesium, and aluminum were wired in sequence and suspended in the test liquid to within ¼" of the bottom of the test solution. An air condenser was then placed above the test liquid and the entire apparatus was placed in a constant temperature heating block controlled to 450° F. plus or minus 1° F. Dry air was then introduced through the inlet tube at a rate of 5 liters per hour for 48 hours. At the end of the test period, the samples were cooled to room temperature. The metal coupons were removed and solvent cleaned to remove soluble deposits, then weighed to determine corrosion losses. The viscosity at 100 and 210° F. was determined. The viscosity changes are expressed as percentage in Table II. The samples were then filtered through coarse filter paper (Eaton-Dikeman Co. Grade E and D 615) by gravity, the deposits were washed with acetone and dried after which the collected-sludge was weighed. The sludge weights are expressed as mg. per 200 ml. sample. The acid value change of the test solution was determined by titration of the tested lubricant and subtraction of the original acid value from the final acid value. Metal corrosion loss was determined by weight difference (plus or minus) in the metal coupons before and after the tests and are reported as mg. per cm.<sup>2</sup> of surface exposure.

TABLE II

Results	Example		P and W spec.
	6	7	
	Lube comprising trimethylol-propane dipelargonate mono heptanoate, 1% by wt. p,p'-dioctyldiphenylamine, 1% PANA	Lube comprising trimethylol-propane dipelargonate mono heptanoate, 2.5 wt. percent diisostearylamine, 1% PANA	
Viscosity change 100° F., percent....	229.8	25.6	50 max.
Acid value change.....	4.44	3.69	Report
Total sludge (mg.).....	2,750	538	-----
Metal corrosion (mg./cm. <sup>2</sup> ):			
Copper.....	-2.86	-0.24	±0.30
Steel.....	+0.02	+0.15	±0.30
Titanium.....	+0.02	+0.14	±0.30
Silver.....	+0.02	+0.13	±0.30
Magnesium.....	-11.85	+0.11	±0.30
Aluminum.....	+0.03	+0.12	±0.30

The superiority of diisostearylamine as an oxidation inhibitor is evident upon review of the above data. It may be seen that the diisostearylamine generates far less sludge, suppresses the acid value change, and metal corrosion remains within tolerable limits in each instance whereas excessive copper and magnesium corrosion are experienced using p,p'-dioctyldiphenylamine.

## EXAMPLES VIII AND IX

In order to demonstrate the difference between a secondary amine oxidation inhibitor of the present invention, diisostearylamine and a linear diakylamine of comparable molecular weight, dioctyldecylamine, comparative tests using these two materials were conducted. The tests were performed by adding to one of two diisodecylazelate samples 1% by weight of diisostearylamine and to the other sample 1% by weight of dioctyldecylamine. After addition of the diamines to the respective samples, they were heated to a temperature of 100° C. At this temperature each of the amines were blended completely into the ester solution. They were then allowed to cool to test for

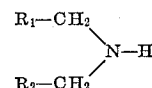
cloud point and pour point with the results as shown below.

Diisodecylazelate.....	99% by weight.....	99% by weight.
Diisostearylamine.....	1% by weight.....	
Dioctyldecylamine.....		1% by weight.
Cloud point.....	-60° F.....	+60° F.
Pour point.....	Less than -70° F.....	+60° F.

It may be readily seen from the above data that diisostearylamine is superior as a lubricant additive that it is compatible with the ester lubricant over a temperature range far in excess of that at which dioctyldecylamine is capable of performing.

I claim:

1. An oxidation inhibitor for a lubricant having the formula:



wherein R<sub>1</sub> and R<sub>2</sub> are branched chain aliphatic hydrocarbon radicals having from 15 to 24 carbon atoms and are the hydrocarbon residue of liquid saturated branched aliphatic acids.

2. The oxidation inhibitor of claim 1 wherein R<sub>1</sub> and R<sub>2</sub> are branched aliphatic hydrocarbon residues of iso-stearic acid.

3. A lubricant composition comprising a major portion of a synthetic ester lubricant together with from 0.1 to 5.0% by weight of the oxidation inhibitor of claim 1.

4. A lubricant composition comprising a major portion of a synthetic ester lubricant together with from 0.1 to 5.0% by weight of the oxidation inhibitor of claim 3.

5. The method which comprises lubricating moving parts of an engine with a synthetic ester lubricant containing the oxidation inhibitor of claim 1.

6. The method which comprises lubricating moving parts of an engine with a synthetic ester lubricant containing the oxidation inhibitor of claim 2.

## References Cited

## UNITED STATES PATENTS

2,166,971	7/1939	Schmidt .....	260—583
2,104,421	1/1938	Grün .....	260—127
2,234,096	3/1941	Teter .....	252—50
1,888,023	11/1932	Adams.....	
2,870,207	1/1959	Niederhauser .....	260—583
3,347,111	3/1966	Oberright .....	252—34.7

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U.S. Cl. X.R.

252—50, 401; 260—583