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Nnadi

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[54] **LUBRICANTS CONTAINING AMINO AND HYDROXY-SUBSTITUTED POLYPHENYLTHIOETHERS**

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[52] **U.S. Cl.**..... **252/47.5,** 252/46.7, 252/47, 252/48.2, 252/48.4, 252/48.6, 252/402, 260/571

[51] **Int. Cl.**..... **C10m 1/42**

[58] **Field of Search**..... 252/47.5, 402

[56] **References Cited**

UNITED STATES PATENTS

2,345,239	3/1944	Cook et al.	252/47.5 X
3,145,177	8/1964	Orloff et al.	252/52
3,156,728	11/1964	Orloff et al.	252/47.5 X
3,285,854	11/1966	Malone	252/47.5 X
3,368,975	2/1968	Davis et al.	252/565

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[57] **ABSTRACT**

Lubricants are stabilized against oxidation and have their EP and detergency properties improved by adding thereto a property improving amount of an amino-substituted polyphenylthioether.

13 Claims, No Drawings

LUBRICANTS CONTAINING AMINO AND HYDROXY-SUBSTITUTED POLYPHENYLTHIOETHERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to improved lubricant compositions. More particularly, it relates to lubricants which have been improved by the addition thereto of an amino and hydroxy-substituted polyphenylthioether.

2. Discussion of the Prior Art

It is well known that many organic liquids and solids used in industrial fluids, such as oils and greases, power transmission fluids and the like, may deteriorate and lose their ability to function when subjected to oxidation. Since these substances are very often used at high temperatures, the rate of oxidative breakdown can be very rapid. This problem is particularly important in the operation of present day automotive and aircraft engines.

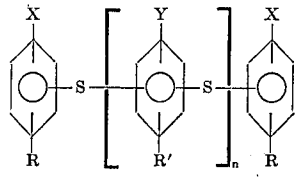
The breakdown of lubricant is almost always accompanied by the formation of sludge, corrosive acids and other products. These can harm the metal surfaces of engines or other machines and interfere with efficient operation of the lubricant.

The ideal way to deal with the problem of oxidation, of course, is to prevent it altogether. Since, however, most additives do not stop oxidation and the formation of potentially harmful solids, much work has also been done to find other materials that can keep the solids from settling on metal surfaces. Usually, therefore, it is necessary to use a combination of additives where oxidation is not entirely stopped - one for retarding oxidation, the other for keeping in suspension those solids resulting from the oxidation that does occur. The art does not expect to find single additives that on the one hand retard oxidation and on the other act as dispensing agents.

No art is known which discloses the compounds disclosed herein as antioxidants or dispersants in lubricants. There is patent art, however, which discloses analogous compounds as lubricants. One of these is U.S. Pat. No. 3,490,737, which teaches a combination of functional fluid and metallic compound. Another is U.S. Pat. No. 3,538,166, disclosing a process for making an analogous thioether which may be used as a functional fluid.

SUMMARY OF THE INVENTION

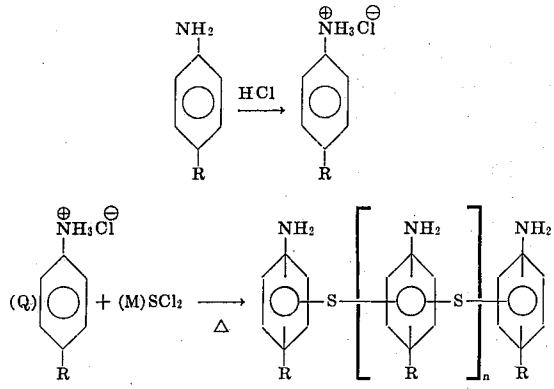
In accordance with the invention, there is provided a lubricant composition comprising a major proportion of a lubricant and an antioxidant or dispersant amount of a compound of the formula



wherein R and R′ are hydrogen, hydrocarbyl of from 1 to 100 carbon atoms, preferably alkyl having from 1 to 100 carbon atoms, preferably from about 4 to 20 carbon atoms, aryl having 6 to 100 carbon atoms or aralkyl having 7 to 100 carbon atoms, and may include in their structure functional groups derived from carboxylic acids, esters, amides, imides, sulfonic and phosphoric acids and derivatives thereof, mercapto, halogeno hydroxyl and cyano. For solubility in oil R, R′ should have greater than two carbon atoms, preferably 4 or more. X and Y are hydroxyl or amino and *n* is from 1 to 10. The X's and Y's and R's and R′ 's may be the same or different. The product may also be a mixture, i.e., where *n* may vary. The most usual mixture will comprise compounds in which *n* is 1, 2, or 3.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In general, the polyphenylthioethers may be prepared in known ways. One method, the method used herein, involves reactions that may be set forth as follows:



Q and M are the equivalents of reactants, varied to give the desired polymeric product. For example the tetramer is obtained when Q is 4 and M is 3.

The amino group may be protected by other reactions such as acetylation or by neutralization with other mineral acids such as HBr, HF, H_2SO_4 or H_3PO_4 or with organic acids such as carboxylic or sulfonic acids. The polymers may then be copolymerized with a phenol and SCl_2 to yield polymers having X as NH_2 and OH. In a variation of the procedure to obtain polymers containing both the NH_2 and OH groups, mixtures of phenol and aniline with the protected NH_2 group or of partially SCl_2-polymerized phenol and aniline with protected NH_2 group may be reacted. Suitable products may be obtained with partially blocked or totally unblocked arylamines as starting materials.

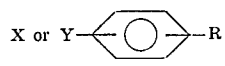
Elemental sulfur, with a promotor, such as a glycol, may be used in place of SCl_2 for sulfurization in part of or all the steps of reaction requiring sulfurization.

It is generally preferable to use a solvent in the reaction. For this purpose, any solvent that is inert to HCl and SCl_2 under reaction conditions may be used as solvent for the process. Some of these are, for example tetrahydrofuran and paraffins.

The reaction temperature can range from 0°C to 300°C with the range between 0° and 180°C preferred. The amine hydrochloride portion of the product can be reconverted to the parent amine by washing the prod-

uct with aqueous solutions of sodium or potassium hydroxides and carbonates or those of calcium, zinc, magnesium and barium. This may also be done by stirring the product with excess amounts of secondary and tertiary alkylamines.

The starting aryl compound for the polymers of this invention are those of the formula

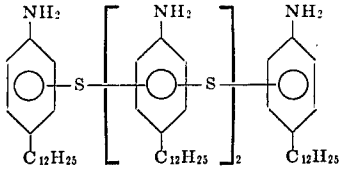


examples of which appear as follows:

X or Y	R
NH_2 or OH	H CH_3 C_4H_9 C_8H_{17} $C_{10}H_{20}$ $C_{20}H_{41}$ C_6H_5 $C_{10}H_7$ $C_6H_5CH_2$ $C_6H_5(CH_2)_{2-10}$

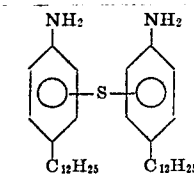
The additives of this invention can be used in a wide variety of lubricant media. They can be used as effective agents in lubricating oils such as mineral oils, both naphthenic and paraffinic, including those containing substantial amounts of aromatic oils, synthetic oils, such as synthetic hydrocarbons obtained by polymerizing olefins, synthetic esters and polysiloxanes and the like. The term "lubricant" also includes greases made by adding a grease forming agent to any of those oils mentioned, but is not meant to include any of the thioethers themselves as lubricants. The thioethers disclosed herein are especially useful in stabilizing a lubricating oil made by reacting an aliphatic monocarboxylic acid containing from 4 to 10, preferably 5 to 9, carbon atoms with pentaerythritol, including mono- and dipenterythritol or mixtures thereof. A widely used lubricating oil is made from monopentaerythritol and a mixed C_5–C_9 acid, preferably C_5 and C_9. For purposes of illustration, the following examples are offered. It is to be remembered they are for illustration only and are not intended to limit the scope of the invention. Parts are by weight.

Example 1



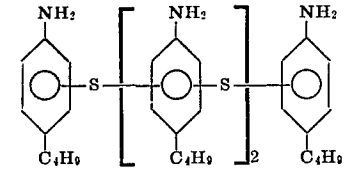
One mole (262 g) of dodecylaniline was dissolved in 262 g of Promor No. 5 process oil and then neutralized with hydrogen chloride gas until the theoretical amount of HCl (36.5 g) was taken up. To the above dodecylaniline hydrochloride was added 76.5 g of sulfur dichloride (about 0.75M) at such a rate as to keep the reaction temperature at 30°–70°C. The temperature was slowly raised to 150°C during a period of 6 hours and kept at 150°C for 4 hours under nitrogen purge. The reaction was cooled, mixed with 500 cc of toluene and 100 cc of tetrahydrofuran and then washed once with 100 cc 10 percent NaOH solution and twice with 250 cc of H_2O. The washed product was distilled to remove the solvents and unreacted dodecylaniline. The final stage of distillation was carried out to a pot temperature of 180°C and 3 mm Hg, where it was held for 2 hours. The yield of product was 509 g. it contained 2.7 percent N and 2.94 percent S and had a total base number of 81. This product consisted mostly of trimer, tetramer and pentamer.

Example 2



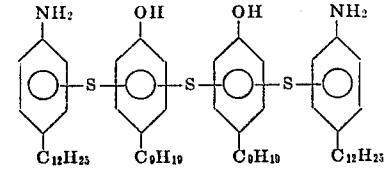
By reacting 600 g (2 moles) of dodecylaniline hydrochloride and 102 g sulfur dichloride (1 mole) in 400 cc of tetrahydrofuran as described in Example 1, 450 g product was obtained. It was necessary to distil off some tetrahydrofuran to increase the reaction temperature to the range indicated in Example 1. The product contained 4.60 percent N, and 7.36 percent S, and had a molecular weight (by vapor pressure lowering) of 467. This is the average molecular weight for the dimer.

Example 3



From 150 g (1 mole) of p-n butylaniline, 35.5 g of $HCl_{(g)}$ (1 mole) and 76.5 g of SCl_2 (0.75 mole) reacted in 400 cc tetrahydrofuran solvent as described in Example 1, 132 g of product was obtained. It contained 5.36 percent N and 8.94 percent S, and had a molecular weight (by vapor pressure lowering) of 649, indicating the tetramer.

Example 4



One mole (220 g) of nonyphenol was dissolved in 300 cc of tetrahydrofuran and reacted with 50 g of SCl_2 (about 0.5 mole) at 35°–50°C. The reaction mixture was slowly raised to 140°C by distilling off some tetrahydrofuran and kept at 150°–160°C under nitrogen purge for 4 hours after which it was cooled to room

temperature. To this product was added 300 g of dodecylaniline hydrochloride dissolved in 300 cc of tetrahydrofuran. Then 101 g SCl_2 was added and the reaction carried out as described in Example 1. The yield of product after holding at 180°C 3 mm Hg for 2 hours was 452 g. To reconvert it to the aniline, the product was dissolved in 200 cc toluene and stirred with about 110 g of triethylamine and filtered. Finally the reaction mixture was again distilled by raising the temperature to and held it at 180°C at 3 mm Hg for 2 hours. The yield of product was 476 g.

EVALUATION OF PRODUCTS

The antioxidant properties of the novel compounds of this invention are measured by adding these compounds to a suitable oil and subjecting the oil to oxidation at high temperatures. The test is a bulk oil catalytic oxidation process in which a stream of dry air is passed through a heated sample of the lubricant compositions for a time at various elevated temperatures in the presence of iron, copper, aluminum and lead as catalysts. The metal samples consist of 15.6 sq. in. of sand-blasted iron wire, 0.78 sq. in. of polished copper wire, 0.87 sq. in. of polished aluminum wire, and 0.167 sq. in. of polished lead surface. The antioxidant activity is evaluated as the ability of the additive to control the acid number and viscosity of the oil and prevent them from rising at an unduly rapid rate. The sludge formation during the oxidation is estimated visually. The base stock is a mixed ester of pentaerythritol prepared by reacting an acid mixture of 1 mole of pelargonic acid and 3 moles of commercial valeric acid with 1 mole of technical grade pentaerythritol or a mineral oil.

The results of this test are tabulated below in separate tables.

OXIDATION TEST IN MIXED ESTER FLUID
(24 hour oxidation)

Inhibitor	Wt. %	Temp., °F.	NN	KV, %	Sludge
None	—	425	5.85	226	Nil
		450	8.25	585	Trace
Example 1	0.5	425	0.90	21	Nil
		450	2.00	57	Nil
	1.0	425	1.20	28	Nil
		450	3.00	57	Nil
Example 2	0.5	425	1.65	25	Light
		450	2.85	60	Light
	1.0	425	0.76	21	Trace
		450	2.25	50	Nil
Example 3	0.5	425	1.6	22	Light
		450	2.8	66	Light
	1.0	425	0.7	12	Trace
		450	2.2	50	Nil
Example 4	0.5	425	4.05	170	Nil
	1.0	425	4.05	114	Nil

OXIDATION TEST IN MINERAL OIL*

Inhibitor	Wt. %	Temp., °F	Oxidation Time, hrs.	NN	KV, %	Sludge
None	—	325	40	17.0	334	Heavy
	—	325	72	24.3	—	Trace
Example 1	2	325	72	1.35	8	Nil
	4	325	72	1.65	13	Light
	4	325	40	1.35	8	Trace
Example 4	5	325	72	3.9	21	Nil

*130 sec Solvent refined paraffinic neutral.

The thioethers disclosed herein were tested as detergents by the Sulfuric Acid Neutralization Test and the Pyruvic Acid Dispersion Test.

The Sulfuric Acid Neutralization Test gives a measure of the ability of detergent additives to neutralize strong acids formed in engines operating on sulfur containing fuels. H_2SO_4 is mixed with a heated blend of the additive and the oil. A solution of this is formed in isooctane which is then centrifuged to separate insolubles. The optical density of the clear solution is then measured. From this value the optical density of the original additive blend diluted to a corresponding amount with isooctane is subtracted. The difference gives the optical density of the dispersed H_2SO_4 reaction products. The optical density of an acetone extraction of the isooctane-oil solution is then determined. The average optical density of the oil-isooctane solution is expressed as the optical density of the dispersed H_2SO_4 reaction product. The average density of the acetone solution is expressed as the optical density of the values or either one alone is used in the evaluation of detergent additives.

The Pyruvic Acid Dispersion Test gives a measure of the dispersant value of additives and serves to predict the performance of detergent additives in engines operating on low sulfur content fuels. When used in combination with the neutralization of H_2SO_4 bench test procedures it serves to predict the performance of detergent additives in engines operating on high sulfur content fuels. Pyruvic acid is mixed with a heated blend of the additive and the oil. The mixture is diluted with benzene and centrifuged to separate insolubles. The insolubles are dissolved in acetone. The optical density of the oil-benzene solution gives the total amount of color. From this value the optical density of the initial additive blend diluted with benzene to a corresponding amount is subtraced. This corrected value is expressed as the optical density of the dispersed pyruvic acid polymer. The optical density of the acetone solution is expressed as the optical density of the non - dispersed pyruvic acid polymer. These values are used in evaluation of the detergent additives.

The table below summarizes the results of the tests run. The higher the percentage of the test run with pyruvic acid, the better the additive, while a lower value in the sulfuric acid test indicates a better additive.

Additive	Wt. %	Sulfuric Acid Test	Pyruvic Acid Test
None	—	0.098	59.6
Example 1	3	0.024	97.3
Example 2	3	0.137	81.9
Example 4	3	0.144	86.5

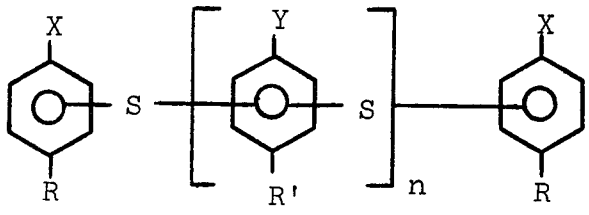
Tests indicated that the thioethers of this invention are also useful as EP agents. The product of Example 1 was placed in a mixed bright and neutral mineral oil stock (62 and 38 percent by volume, respectively) having a viscosity of 481 SUS at 100°F and 63 SUS at 210°F. The test was run in the well known Shell Four-Ball Test at a 60 kg load at 100°F. for 30 minutes, with the following results:

Concentration Wt. %	Wear Scar Diameter (mm) 500 rpm	1000 rpm
—	0.72	0.93
1.0	0.50	0.60

In using the thioethers of the invention as antioxidants, dispersants or EP agents, the concentration may be selected from the range of from about 0.001 to about 20 percent by weight, preferably from about 1 to about 5 percent.

I claim:

1. A lubricating oil or grease composition comprising a major proportion of said lubricating oil or grease and an antioxidant or dispersant amount of a compound of the formula



wherein R and R′ are hydrogen or hydrocarbyl containing from 1 to 100 carbon atoms, X and Y are selected from the group consisting of amino and hydroxy, such that said X and Y are never all amino or all hydroxy, and n is from zero to 10, or mixtures of such compounds.

2. The composition of claim **1** wherein the compound is present in the range of from about 0.001 to about 20 percent by weight.

3. The composition of claim **1** wherein the lubricant is a lubricating oil.

4. The composition of claim **1** wherein the lubricant comprises a grease.

5. The composition of claim **3** wherein the lubricating oil is a mineral lubricating oil.

6. The composition of claim **3** wherein the lubricating oil is a synthetic lubricating oil.

7. The composition of claim **6** wherein the synthetic lubricating oil is an ester of an aliphatic monocarboxylic acid of from 4 to 10 carbon atoms, and mixtures thereof, and pentaerythritol.

8. The composition of claim **7** wherein the acid is a mixture of pelargonic and valeric acids.

9. The composition of claim **1** wherein R and R′ are dodecyl, X is NH_2 and *n* is 2.

10. The composition of claim **1** wherein R and R′ are dodecyl, X is NH_2 and *n* is zero.

11. The composition of claim **1** wherein R is dodecyl, R′ is nonyl, X is NH_2, Y is OH and *n* is 2.

12. The composition of claim **1** wherein the hydrocarbyl is alkyl having from 1 to 100 carbon atoms, aryl having from 6 to 100 carbon atoms and aralkyl having from 7 to 100 carbon atoms.

13. The composition of claim **12** wherein the alkyl contains from 4 to 20 carbon atoms.

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