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3,647,752

TREATMENT OF POLYPHENYL THIOETHERS

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8 Claims

ABSTRACT OF THE DISCLOSURE

The oxidative stability of polyphenyl thioethers is increased and their corrosiveness towards metals is decreased by contacting the polyphenyl thioethers under basic conditions in the liquid phase with an oxidizing agent which maintains its oxidation functionality under basic conditions. For example, m-bis(phenylmercapto) benzene is contacted with a basic aqueous solution of sodium hypochlorite at 100° C. for 8 hours to improve its oxidative stability.

This invention relates to the treatment of certain polyphenyl thioethers which can also be classed as polyphenyl sulfides, which term is meant to include polyphenyl sulfides in which one or more, but not all of the sulfur atoms have been replaced with oxygen atoms, to improve their oxidative stability and to decrease their corrosiveness to metals.

Because of the wide variety of applications under which functional fluids are utilized, a concurrence of many properties, both physical and chemical, are needed in a particular fluid to provide the service demanded. One of the most rigorous demands on fluids is made by gas turbine aircraft hydraulic systems and gas turbine engine lubrication systems. As the speed and altitude of operation of jet powered aircraft increases, lubrication problems also increase because of higher operating temperatures and higher bearing pressures resulting from the increased thrust needed to obtain higher speeds and altitudes. As the service conditions encountered become increasingly severe, the useful life of the functional fluid is, of course, shortened.

Polyphenyl thioethers have been proposed as compounds which can be employed as functional fluids in many different types of application, such as hydraulic fluids, damping fluids, synthetic lubricants, particularly as gas turbine lubricants and atomic reactor coolants.

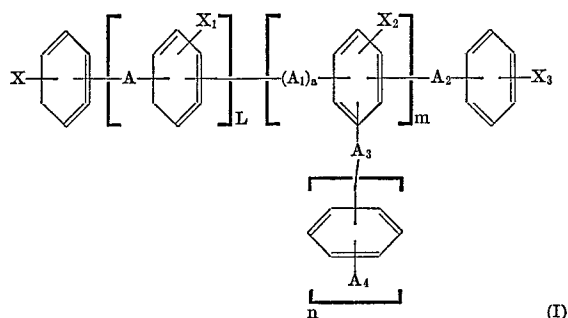
The useful life of any lubricant or hydraulic fluid can be adjudged on the basis of many criteria such as the extent of viscosity increase, the extent of corrosion to metal surfaces in contact with the lubricant and the extent of engine deposits.

It has now been found that the oxidative stability and thus the useful life of polyphenyl thioethers can be greatly extended, even under the severe conditions encountered in jet engines and other devices operating at temperatures of the order of 500° F. and higher, by contacting such thioethers in the liquid phase with an oxidizing agent as hereinafter described. Also, by the process of this invention, the corrosiveness of such thioethers toward certain metals is significantly reduced.

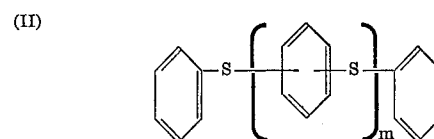
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It is, therefore, an object of this invention to provide a method for increasing the oxidation resistance of polyphenyl thioethers and compositions thereof. Another object is to provide polyphenyl thioethers and compositions thereof which have decreased metal attack and give decreased formation of deposits.

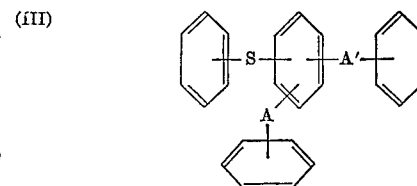
As used herein the term "polyphenyl thioether" includes a compound or physical mixture of compounds represented by the formula:



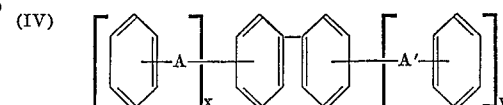
wherein A, A₁, A₂ and A₃ are each a chalcogen having an atomic number of 8 or 16, provided at least one of A, A₁, A₂ and A₃ has an atomic number of 16, X, X₁, X₂, X₃ and X₄ each are selected from the group consisting of hydrogen, alkyl, haloalkyl, halogen, arylalkyl and substituted arylalkyl, L, m and n are whole numbers each having a value of from 0 to 8 and a is a whole number having a value of from 0 to 1 provided that when a is 0, m is a whole number having a value of from 1 to 2. Typical examples of such polyphenyl thioethers are:



where m is a whole number from 0 to 6,



where A and A' are each selected from oxygen and sulfur;



where x and y are whole numbers from 0 to 3 and the sum of x+y is from 1 to 6 and A and A' are each selected

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from oxygen and sulfur but at least one of A and A' is sulfur.

Specific examples of polyphenyl thioethers are:

2-phenylmercapto-4'-phenoxydiphenyl sulfide
 2-phenylmercapto-3'-phenoxydiphenyl sulfide
 2-phenoxy-3'-phenylmercaptodiphenyl sulfide
 3-phenoxy-4'-phenylmercaptodiphenyl sulfide
 2-phenoxy-4'-phenylmercaptodiphenyl sulfide
 2-phenoxy-2'-phenylmercaptodiphenyl sulfide
 o-bis(phenylmercapto)benzene
 p-bis(phenylmercapto)benzene
 Phenylmercaptodiphenyl
 3,3'-bis(phenylmercapto)biphenyl
 3-phenylmercapto-3'-(phenoxy)biphenyl
 Bis(o-phenylmercaptophenyl) sulfide
 Bis(p-phenylmercaptophenyl) sulfide
 Bis(m-phenylmercaptophenyl) sulfide
 1,2,3-tris(phenylmercapto)benzene
 1-phenylmercapto-2,3'-bis(phenoxy)benzene
 1,3-phenylmercapto-5-phenoxybenzene
 1,2,4-tris(phenylmercapto)benzene
 1,3,5-tris(phenylmercapto)benzene
 o-bis(o-phenylmercaptophenylmercapto)benzene
 p-bis(o-phenylmercaptophenylmercapto)benzene
 p-bis(m-phenylmercaptophenylmercapto)benzene
 m-bis(p-phenylmercaptophenylmercapto)benzene
 o-bis(p-phenylmercaptophenylmercapto)benzene
 ar-bis(phenylmercapto)-ar'-(phenylmercapto)benzene
 2,2'-bis(phenylmercapto)diphenyl ether
 2,3'-bis(phenylmercapto)diphenyl ether
 2,4'-bis(phenylmercapto)diphenyl ether
 4,4'-bis(m-tolylmercapto)diphenyl ether
 3,3'-bis(m-tolylmercapto)diphenyl ether
 2,4'-bis(m-tolylmercapto)diphenyl ether
 3,4'-bis(m-tolylmercapto)diphenyl ether
 3,3'-bis(p-tolylmercapto)diphenyl ether
 3,3'-bis(xylylmercapto)diphenyl ether
 4,4'-bis(xylylmercapto)diphenyl ether
 3,4'-bis(xylylmercapto)diphenyl ether
 3,4'-bis(m-isopropylphenylmercapto)diphenyl ether
 3,3'-bis(m-isopropylphenylmercapto)diphenyl ether
 2,4'-bis(m-isopropylphenylmercapto)diphenyl ether
 3,4'-bis(p-tert-butylphenylmercapto)diphenyl ether
 4,4'-bis(p-tert-butylphenylmercapto)diphenyl ether
 3,3'-bis(p-tert-butylphenylmercapto)diphenyl ether
 3,3'-bis(m-di-tert-butylphenylmercapto)diphenyl ether
 3,3'-bis(m-chlorophenylmercapto)diphenyl ether
 4,4'-bis(m-chlorophenylmercapto)diphenyl ether
 3,3'-bis(m-trifluoromethylphenylmercapto)diphenyl ether
 4,4'-bis(m-trifluoromethylphenylmercapto)diphenyl ether
 3,4'-bis(m-trifluoromethylphenylmercapto)diphenyl ether
 2,3'-bis(m-trifluoromethylphenylmercapto)diphenyl ether
 3,3'-bis(p-trifluoromethylphenylmercapto)diphenyl ether
 3,3'-bis(o-trifluoromethylphenylmercapto)diphenyl ether
 3,3'-bis(m-methoxyphenylmercapto)diphenyl ether
 3,4'-bis(m-isopropoxyphenylmercapto)diphenyl ether
 3,4'-bis(m-perfluorobutylphenylmercapto)diphenyl ether
 2-m-tolyloxy-2'-phenylmercaptodiphenyl sulfide
 2-p-tolyloxy-3'-phenylmercaptodiphenyl sulfide
 2-o-tolyloxy-4'-phenylmercaptodiphenyl sulfide
 3-m-tolyloxy-3'-phenylmercaptodiphenyl sulfide
 3-m-tolyloxy-4'-phenylmercaptodiphenyl sulfide
 4-m-tolyloxy-4'-phenylmercaptodiphenyl sulfide
 3-xylyloxy-4'-phenylmercaptodiphenyl sulfide
 3-xylyloxy-3'-phenylmercaptodiphenyl sulfide
 3-phenoxy-3'-m-tolylmercaptodiphenyl sulfide
 3-phenoxy-4'-m-tolylmercaptodiphenyl sulfide
 2-phenoxy-3'-p-tolylmercaptodiphenyl sulfide
 3-phenoxy-4'-m-isopropylphenylmercaptodiphenyl sulfide
 3-phenoxy-3'-m-isopropylphenylmercaptodiphenyl sulfide
 3-m-toloxo-3'-m-isopropylphenylmercaptodiphenyl sulfide
 4-m-trifluoromethylphenoxy-4'-phenylmercaptodiphenyl sulfide

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3-m-trifluoromethylphenoxy-4'-phenylmercaptodiphenyl sulfide

2-m-trifluoromethylphenoxy-4'-phenylmercaptodiphenyl sulfide

5 3-m-trifluoromethylphenoxy-3'-phenylmercaptodiphenyl sulfide

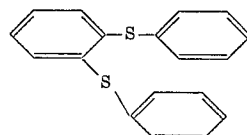
3-p-chlorophenoxy-3'-phenylmercaptodiphenyl sulfide and 3-m-bromophenoxy-4'-phenylmercaptodiphenyl sulfide.

10 Mixtures of polyphenyl thioethers can also be treated according to the method of this invention. A typical example of a mixture of polyphenyl thioethers is one which contains by weight from about 45% to about 55% m-phenoxyphenyl-m-phenylmercaptophenyl sulfide, from about 25% to about 35% bis(m-phenylmercaptophenyl) sulfide and from about 18% to about 25% bis(m-phenoxyphenyl) sulfide.

Preferred polyphenyl thioethers of this invention are mixtures comprising m-bis(phenylmercapto)benzene and certain other materials which have properties that make them well suited for the uses disclosed above and particularly those applications, such as jet engine lubricants, requiring thermal and oxidative stability and wide liquid range.

25 Such other materials can advantageously be employed in amounts of from about 20 to about 200 parts by weight per 100 parts of m-bis(phenylmercapto)benzene. The other materials contemplated to be used with m-bis(phenylmercapto)benzene to provide such preferred mixtures are as follows:

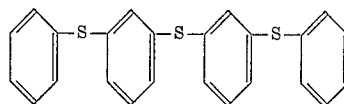
30 (a) The three-, four-, five- and six-ring polyphenyl thioethers, for example, o-bis(phenylmercapto)benzene (V)



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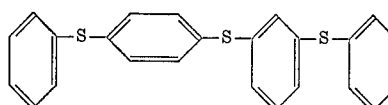
bis(m-phenylmercaptophenyl) sulfide

40 (VI)



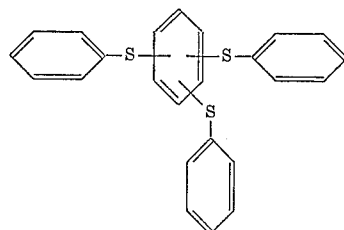
m - phenylmercaptophenyl-p-phenylmercaptophenyl sulfide

45 (VII)



50 the trisphenylmercaptobenzenes

(VIII)

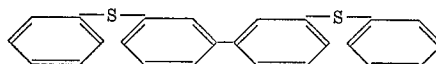


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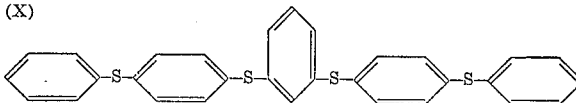
such as 1,2,4-trisphenylmercaptobenzene, 3,3'-bis(phenylmercapto)biphenyl

65 (IX)



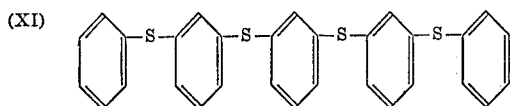
m-bis(p-phenylmercaptophenylmercapto)benzene,

70 (X)



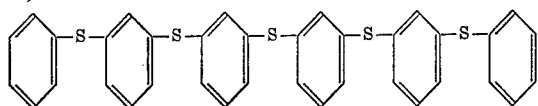
75 m-bis(m-phenylmercaptophenylmercapto)benzene,

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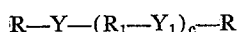


and bis[m - (m-phenylmercaptophenylmercapto)phenyl] sulfide,

(XII)

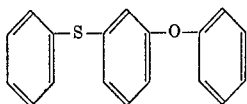


(b) The mixed polyphenyl oxy-thioethers having the formula



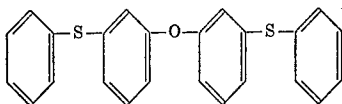
wherein R is a phenyl group, R₁ is a phenylene group and Y and Y₁ are each selected from the group consisting of oxygen and sulfur, providing at least one of Y and Y₁ is sulfur and c is a whole number from 1 to 5. Examples of such mixed polyphenyl oxythioethers are m-phenylmercaptodiphenyl ether

(XIII)



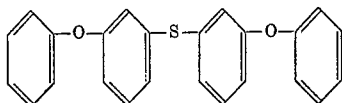
3,3'-bis((phenylmercapto)diphenyl ether,

(XIV)



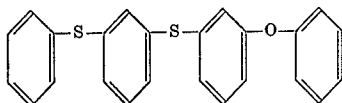
3,3'-bis(phenoxy)diphenyl sulfide,

(XV)



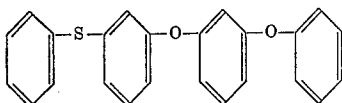
3-phenoxy-3'-phenylmercaptodiphenyl sulfide,

(XVI)



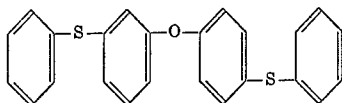
3-phenylmercapto-3'-phenoxydiphenyl ether,

(XVII)



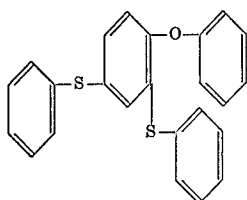
3,4'-bis(phenylmercapto)diphenyl ether

(XVIII)



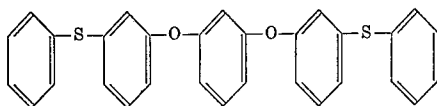
1-phenoxy-2,4-bis(phenylmercapto)benzene

(XIX)



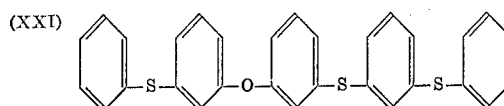
m-bis(m-phenylmercaptophenoxy) benzene,

(XX)



and 3-phenylmercapto-3'-(m-phenylmercaptophenylmercapto)diphenyl ether,

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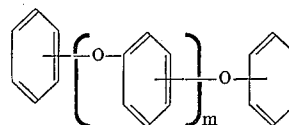


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(c) The four-, five- and six-ring polyphenyl ethers which can be represented by the structure

(XXII)

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where m is 2, 3 or 4 such as bis(m-phenoxyphenyl) ether, m-phenoxyphenyl p-phenoxyphenyl ether, m-bis(m-phenoxyphenoxy) benzene, m-[(m-phenoxyphenoxy) (p-phenoxyphenoxy)]benzene, p-[(p-phenoxyphenoxy) (m-phenoxyphenoxy)]benzene, p-bis(m-phenoxyphenoxy)benzene, m-bis(p-phenoxyphenoxy)benzene and o-bis(m-phenoxyphenoxy)benzene and combinations of (a) through (c). Compounds of (a) and (b) above are also contemplated to be employed alone or in combination

with each other and (c) in the process of this invention.

The oxidizing agents which can be employed in the process of this invention are those oxidizing agents which will retain their oxidation functionality under basic conditions (as hereinafter described). Typical examples of such agents are sodium and calcium hypochlorite, sodium chlorite, chlorine dioxide, hydrogen peroxide, sodium, calcium and zinc peroxide, sodium, potassium and ammonium perborate, potassium permanganate, peroxyacetic acid, tert-butyl peroxide and benzoyl peroxide.

In carrying out the process of this invention, improved polyphenyl thioethers are prepared by contacting the thioethers as described above with an aqueous solution of the agent under basic conditions by means known to the art for contacting liquids with liquids, e.g., by agitating a mixture of the thioether and the solution of oxidizing agent. In many cases, depending upon the oxidizing agent utilized, it is convenient to first dissolve the oxidizing agent in water, followed by the addition of sodium or potassium hydroxide or other strong base, to bring the pH of the resulting solution in the range of about 9-13. The resulting solution is then utilized to treat the thioether. The thioether can be recovered after treatment by means known to the art, for example, by filtration or by distillation under reduced pressure.

Generally the improvements obtained by the process of this invention are unaffected by the concentration of the oxidizing agent and the time of contact; however, it should be realized that there are minimum values of concentration and time below which the process of this invention becomes impractical. A minimum concentration of oxidizing agent of about 65% by weight of polyphenyl thioether to be treated should be used. The length of time of contact will vary depending upon variances in temperature and the concentration of the contacting agent but a minimum time of about one-quarter hour at about 50° C. should be used. In general, times in the order of 1 to 15 hours are sufficient for most conditions.

The temperature at which the process of this invention is carried out should be above about 50° C. up to about 110° C. The choice of a particular temperature will be dictated, for example, by time available, by the facilities available, the concentration of the contacting agent and the characteristics of the thioether being treated. For example, when using the oxidizing agent in amounts of from 2 to 3% by weight of the thioether a contact period of from about 5 to 10 hours at temperatures in the range of about 75°-100° C. provide the optimum efficiency of equipment and benefit to the fluid without degradation of thioether, as by forming the sulfoxide or sulfone of said thioether.

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The mechanism through which the improvements in the properties of the esters treated according to the method of this invention occurs is not completely understood at this time. Particularly unexpected is the improvement in the oxidative stability of the above-described fluids brought about by the process of this invention. It has been found, however, that the combined oxidation-saponification treatment is superior to either oxidation or saponification alone.

The following non-limiting examples illustrate the process of this invention.

EXAMPLE 1

Into a five-liter flask fitted with a thermometer, heater, reflux condenser, agitator and a pH meter there was charged 2000 grams of m-bis(phenylmercapto)benzene, 1000 grams of a 4-6% sodium hypochlorite solution, 50 grams of sodium hydroxide pellets and 950 grams of water. The resulting mixture was heated (the initial pH was about 13.3) with stirring, to 100° C. at which time the pH of the mixture was about 11. The mixture was then held at 100° C. for eight hours (with stirring) with additional sodium hypochlorite being added whenever there was an indication (by potassium iodide paper) that hypochlorite ion was no longer present. A total of an additional 450 grams of the sodium hypochlorite solution was added during the eight hour hold period. The batch was allowed to cool overnight resulting in the formation of water and oil layers. The layers were separated and the oil layer was washed three times with about 2000 ml. each time of hot water. The water washes were combined and extracted with 300 ml. of benzene. The benzene extracts and the oil layer were combined and dehydrated (to 130° C.) under vacuum and the residue distilled (to 250° C.) to provide about 1900 grams of treated m-bis(phenylmercapto)benzene.

EXAMPLE 2

Generally following the procedure of Example 1 except omitting the sodium hydroxide, 2000 grams of m-bis(phenylmercapto)benzene and 1000 grams of 4-6% sodium hypochlorite were heated at about 90° C. for about eight hours with the addition of 800 ml. of the hypochlorite solution during the heating period so as to maintain a positive potassium iodide test, washed and distilled.

EXAMPLE 3

Generally following the procedure of Example 1 except omitting the sodium hypochlorite, 1548 grams of m-bis(phenylmercapto)benzene were heated with 83 grams of 98% sodium hydroxide and 1548 grams of water at 100° C. for about eight hours, washed and distilled.

The treated fluid from the above examples was tested in a recognized bench test to determine its oxidative stability and corrosiveness to metal. The results of these tests are reported in Table I.

The data reported in Table I was obtained by employing the procedure described in Federal Test Specification 791, Method 5308, except that the fluid tested was heated to a temperature of 500° F. for a period of 48 hours instead of 250° F. for 168 hours as specified in said method, in the presence of certain metals and air. The viscosity increase of the fluid is determined as well as information as to the corrosiveness of the test fluid to metals. In order to demonstrate the effectiveness of the process of this invention in improving the oxidative stability and reduced corrosiveness of the fluids, samples of the fluid treated as described above and on an untreated sample of the same fluid (control) were tested. The metal specimens used were steel, copper, silver, titanium, magnesium alloy and aluminum alloy. However, only the results upon copper and silver are reported since the untreated fluid tested had essentially no effect

on steel, magnesium alloy, titanium and aluminum alloy. Viscosity measurements were made according to ASTM Method D-445-53T using a Cannon-Fenske modified Ostwald viscosimeter. The percent viscosity increase was determined by measuring the viscosity of the samples before and after the test, dividing the difference by the original viscosity and multiplying the quotient by 100. The corrosiveness to metals was determined by weighing metal specimens of known size before and after the test.

TABLE I

Ex. No.	Percent viscosity increase at 100° F.	Metal attack, mg./cm. ²		Decrease in metal attack, percent	
		Cu	Ag	Cu	Ag
Control	8.5	-3.3	-1.9		
1	3.2	-1.7	-0.9	48.5	52.7
2		-3.0	-1.7	9.1	10.7
Control	18.9	-4.1	-3.3		
3	14.5	-3.5	-2.2	14.3	33.4

From the data in Table I above the reduction in viscosity increase indicates the increased oxidative stability of polyphenyl thioethers and the reduction in corrosiveness to copper and silver brought about by treating such thioethers according to the process of this invention. Thus, the useful life of the polyphenyl thioethers is improved according to the process of this invention.

While this invention has been described with respect to various specific examples of embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for improving the oxidative stability and to decrease the corrosiveness to metals of polyphenyl thioethers which comprises contacting at a temperature of from about 50° C. to about 110° C., in the liquid phase and under basic conditions, a polyphenyl thioether with an aqueous solution of an oxidizing agent which maintains its oxidative function under basic conditions, for a period of time sufficient to improve the oxidative stability and to decrease the corrosivity to metals of the polyphenyl thioether.

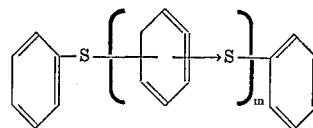
2. The process of claim 1 where the contacting is at a pH of about 9.

3. The process of claim 1 where the oxidizing agent is an alkali metal hypochlorite.

4. The process of claim 3 where the oxidizing agent is sodium hypochlorite.

5. The process of claim 4 wherein the polyphenyl thioether is m-bis(phenylmercapto)benzene.

6. The process of claim 1 wherein the polyphenyl thioether is represented by the formula:



where m is a whole number from 0 to 6.

7. The process of claim 6 wherein the polyphenyl thioether is m-bis(phenylmercapto)benzene.

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8. The process of claim 1 wherein the polyphenyl thioether is a mixture comprising, by weight, from about 42% to about 99% m-bis(phenylmercapto)benzene and from about 17% to about 58% of a mixture comprising, by weight, from about 20% to about 35 bis(m-phenylmercaptophenyl) sulfide, from about 40% to about 60% 3-phenoxy-3'-phenylmercaptodiphenyl sulfide and from about 20% to about 30% bis(m-phenoxyphenyl) sulfide and the oxidizing agent is sodium hypochlorite.

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5 ALEX MAZEL, Primary Examiner

D. R. PHILLIPS, Assistant Examiner

U.S. Cl. X.R.

10 252—45, 48.2, 48.4; 260—609 F