

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to ester-based, in particular diester and polyol ester-based turbo oils which exhibit superior antioxidancy and reduced deposit forming tendencies. More particularly it is related to turbo oils comprising esters of pentaerythritol with fatty acids as basestock, and containing a combination of additives which impart improved antioxidancy and reduced deposit formation.

Description of the Related Art

Organic compositions such as mineral oils and lubricating compositions are subject to deterioration by oxidation and in particular are subject to such deterioration at high temperatures in the presence of air. This deterioration often leads to buildup of insoluble deposits which can foul engine parts, deteriorate performance, and increase maintenance. This is particularly the case for lubricating oils used in jet aircraft where wide temperature ranges and extreme operating conditions are likely to be encountered. Proper lubrication of aircraft gas turbines, for example, requires the ability to function at bulk oil temperatures as low as -65°F to as high as 450-500°F.

Most lubricants contain additives to inhibit their oxidation. For example, U.S. Patent No. 3,773,665 discloses a lubricant composition containing an antioxidant additive mixture of dioctyl diphenylamine and a substituted naphthylamine. U.S. Patent Nos. 3,759,996; 3,573,206; 3,492,233, and 3,509,214 disclose various methods of oxidatively coupling alkylated diphenylamines with substituted naphthylamines.

Patents disclosing the use of tri-substituted triazines in lubricants generally demonstrate the antioxidant function of these molecules when either used alone, or in combination with other antioxidants. They do not describe the use of these materials as anti-deposition additives. U.S. Patent 3,250,708 describes the use of several triazine derivatives, and combinations with hydroxyl aromatic co-antioxidants. U.S. Patent 3,278,436 and 3,322,763 describes tri-substituted triazines including piperidiny1 bridged triazines in combination with hydroxyl aromatics.

European Patent application 002,269 discloses the use of tri-substituted triazines where at least one of the amino substituents contains at least one hydrogen as antioxidants, and in combination with arylamine antioxidants.

U.S. Patent 3,642,630 discloses the use of symmetrical and asymmetrical substituted triazines with N-substituted phenothiazine imparts good oxidation stability to synthetic ester based lubricants over a wide range of temperatures.

Other triazine derivatives disclosed in a number of patents to stabilize oils would not be suitable for use in aviation turbine oils as these derivatives contain halogens which are corrosive to metals. For example, U.S. Patent 3,198,797 utilizes 2,4-dichloro-6-dialkyl-dihydroxy-anilino-1,3,5 triazines. Similarly, U.S. Patent 3,202,681 utilizes monohalogen substituted triazines, especially monochloro substituted ones.

U.S. Patent 4,140,643 discloses nitrogen- and sulfur-containing compositions that are prepared by reacting a dimercaptiothiadiazole (DMTD) with oil-soluble dispersant and subsequently reacting the intermediate thus

formed with carboxylic acid or anhydride containing up to 10 carbon atoms having at least one olefinic bond. The resulting compositions are claimed to be useful in lubricants as dispersant, load-carrying additive, corrosion inhibitor, and inhibitors of Cu corrosivity and lead paint deposition.

U.S. Patent 5,055,584 discloses maleic derivative of DMTD to be used as antiwear and antioxidant in lubricating composition.

U.S. Patent 4,193,882 is directed to improved corrosion inhibiting lube composition that contains the reaction product of DMTD with oleic acid.

Other references which teach the use of DMTD derivatives in lube composition to improve one or several of performance features (antiwear, extreme pressure, corrosion inhibition, antioxidancy) are EP 310 366-B1, U.S. 2,836,564, U.S. 5,126,396, U.S. 5,205,945, U.S. 5,177,212 and U.S. 5,278,751.

It has been discovered that the deposit forming tendencies and antioxidant properties of the basic antioxidant systems of the prior art, e.g., tri-substituted triazines alone or in combination with arylamines, can be greatly enhanced by the addition of a small amount of a sulfur containing additive, specifically derivatives of dimercaptiothiadiazole (DMTD).

SUMMARY OF THE INVENTION

The present invention resides in a turbo oil composition exhibiting enhanced antioxidancy and resistance to deposit formation, and to a method for achieving that result in turbo oils.

The gas turbine lubricating oil of the present invention comprises a major proportion of synthetic polyol ester based base stock including diesters and polyol esters, preferably polyol ester based base stock and a minor proportion of an antioxidant/deposit control additive comprising a non-sulfur containing, triazine derivative antioxidant and DMTD or its substituted derivatives. Other, conventional additives such as extreme pressure, pour point reduction, oxidative stability, anti-foaming, hydrolytic stability, improved viscosity index performance, anti-wear, and corrosion inhibitor additives and others may also be employed.

Improved oxidation and deposit control performance in turbo lube oils is achieved by adding to the synthetic polyol ester based lubricating oil an additive package containing a mixture of a non-sulfur containing triazine antioxidant and DMTD, a DMTD derivative or mixtures thereof.

The non-sulfur containing triazine antioxidant is used in an amount in the range 0.1 to 1.2 percent by weight, preferably 0.2 to 0.9 percent, most preferably 0.4 to 0.7 percent, while the DMTD a DMTD derivative or mixture thereof is used in an amount in the range 50 to 1000 ppm, preferably 100 to 600 ppm, most preferably 200-500 ppm.

The non-sulfur containing triazine antioxidant and 2,5-dimercapto-1,3,4-thiadizole (DMTD), its derivatives or mixtures thereof are used in a ratio in the range of 2:1 to 100:1, preferably 5:1 to 40:1, most preferably 8:1 to 20:1.

The use of a non-sulfur containing triazine antioxidant and DMTD, DMTD derivative or mixtures thereof produces a turbo oil exhibiting markedly

superior oxidation and deposit control properties performance as compared to the performance exhibited without the combination.

DETAILED DESCRIPTION

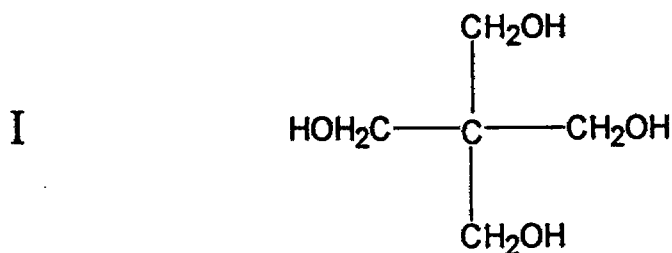
A turbo oil having unexpectedly superior deposition performance comprises a major portion of a synthetic polyol ester base oil and minor portion of an anti-deposition additive package consisting of a mixture of a non-sulfur containing substituted triazine derivative with DMTD, DMTD derivatives or mixtures thereof. Synthetic esters include diesters and polyol esters.

The diesters that can be used for the improved deposition turbo oil of the present invention are formed by esterification of linear or branched C₆-C₁₅ aliphatic alcohols with one of such dibasic acids as adipic, sebacic, or azelaic acids. Examples of diesters are di-2-ethylhexyl sebacate and dioctyl adipate.

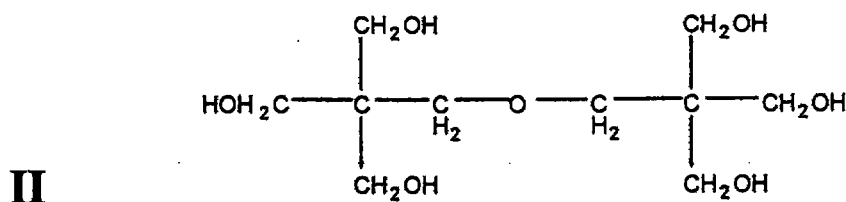
The synthetic polyol ester base oil is formed by the esterification of an aliphatic polyol with carboxylic acid. The aliphatic polyol contains from 4 to 15 carbon atoms and has from 2 to 8 esterifiable hydroxyl groups. Examples of polyol are trimethylolpropane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol and mixtures thereof.

The carboxylic acid reactant used to produce the synthetic polyol ester base oil is selected from aliphatic monocarboxylic acid or a mixture of aliphatic monocarboxylic acid and aliphatic dicarboxylic acid. The carboxylic acid contains from 4 to 12 carbon atoms and includes the straight and branched chain aliphatic acids, and mixtures of monocarboxylic acids may be used.

The preferred polyol ester base oil is one prepared from technical pentaerythritol and a mixture of C₄-C₁₂ carboxylic acids. Technical pentaerythritol is a mixture which includes about 85 to 92% monopentaerythritol and 8 to 15% dipentaerythritol. A typical commercial technical pentaerythritol contains about 88% monopentaerythritol having the formula



and about 12% of dipentaerythritol having the formula



The technical pentaerythritol may also contain some tri and tetra pentaerythritol that is normally formed as by-products during the manufacture of technical pentaerythritol.

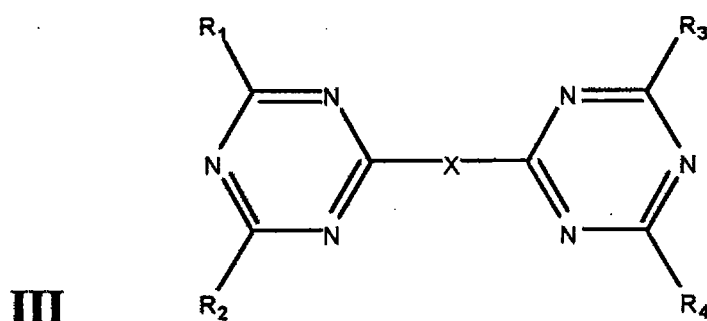
The preparation of esters from alcohols and carboxylic acids can be accomplished using conventional methods and techniques known and familiar to those skilled in the art. In general, technical pentaerythritol is heated with the desired carboxylic acid mixture optionally in the presence of a catalyst. Generally, a slight excess of acid is employed to force the reaction to completion. Water is removed during the reaction and any excess acid is then stripped from the reaction mixture. The esters of technical pentaerythritol may be used

without further purification or may be further purified using conventional techniques such as distillation.

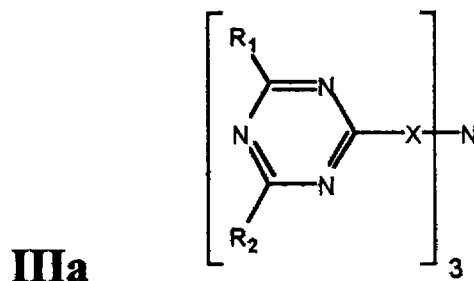
For the purposes of this specification and the following claims, the term "technical pentaerythritol ester" is understood as meaning the polyol ester base oil prepared from technical pentaerythritol and a mixture of C₄-C₁₂ carboxylic acids.

As previously stated, to the polyol ester base stock is added a minor portion of an additive mixture comprising a non-sulfur containing triazine derivative and DMTD, a DMTD derivative or mixtures thereof.

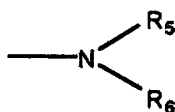
The non-sulfur containing triazine derivatives are preferably those of the form:



Or alternatively, compound III may also be of the form:



where R₁, R₂, R₃, R₄ are the same or different and are

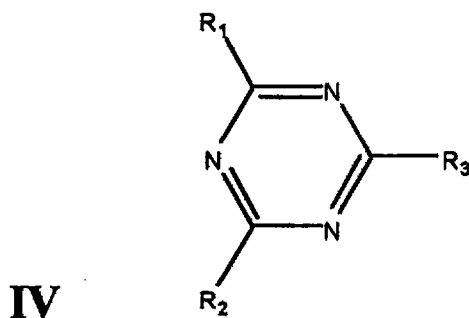


wherein R₅ and R₆ are the same or different and are selected from the group consisting of C₂ to C₁₆ branched or straight chain alkyl, aryl-R₇ where R₇ is branched or straight chain C₂ to C₁₆ alkyl, cyclohexyl-R₇ where R₇ is H or branched or straight chain C₂ to C₁₆ alkyl, and mixtures thereof. Preferably R₁, R₂, R₃, and R₄ are the same or different and are all dialkyl amino groups where the alkyl chains are C₄ to C₁₂ and mixtures thereof.

For compound III, X is a bridging group which is selected from the group consisting of piperidino, hydroquinone, NH-R₈-NH and mixtures thereof where R₈ is C₁ to C₁₂ branched or straight chain alkyl and mixtures thereof.

For compound IIIa, X is selected from the group consisting of piperidino, hydroquinone, NH-R₈ and mixtures thereof where R₈ is C₁ to C₁₂ branched or straight chain alkyl and mixtures thereof.

The triazine derivative may also be of the form:

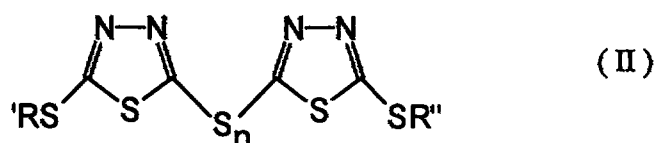
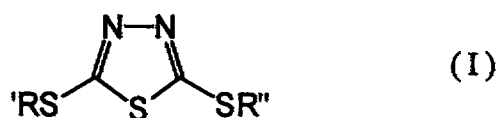


where R₁, R₂, and R₃ are identical to the description above. The preferred non-sulfur containing triazines are those of the formula III and IIIa. Those of formula IV are less preferred due to their lower molecular weight which leads to higher volatility and poorer suitability for high-temperature synthetic oil use.

The non-sulfur containing triazine antioxidant is used in an amount in the range 0.1 to 1.2 percent by weight (based on polyol ester base stock), preferably 0.2 to 0.9 percent, most preferably 0.4 to 0.7 percent.

As previously stated, to the synthetic oil base stock is added a minor portion of an additive comprising a mixture of a triazine derivative and DMTD or its derivatives or mixtures thereof. The DMTD derivatives referred to here include "capped" DMTD, where both mercaptans are reacted with various functional groups, and the dimer of the capped DMTD.

The sulfur containing additives used in this invention include DMTD and the capped DMTD derivative (I) and the dimer (II) of the capped or uncapped DMTD (collectively referred to hereinafter and in the claims as DMTD), which are described by the structural formula:



where R' and R'' are the same or different and are hydrogen, alkyl, cycloalkyl, alkyl-substituted cycloalkyl, aryl, alkylester, alkyl ether and mixtures thereof wherein R' and R'' in total contain 30 carbons or less and $n = 1-2$. Preferably R' or R'' is H, most preferably both are H.

The mixture of non-sulfur containing triazine antioxidant and DMTD, substituted derivatives of DMTD and mixtures thereof are used in a

ratio in the range of 2:1 to 100:1, preferably 5:1 to 40:1, most preferably 8:1 to 20:1.

The reduced-deposit oil, preferably synthetic polyol ester-based reduced-deposit oil may also contain one or more of the following classes of additives: antifoamants, antiwear agents, corrosion inhibitors, hydrolytic stabilizers, metal deactivator, detergents and additional antioxidants. Total amount of such other additives can be in the range .5 to 15 wt%, preferably 2 to 10 wt%, most preferably 3 to 8 wt%.

Antioxidants which can be used include aryl amines, e.g. phenyl-naphthylamines and dialkyl diphenyl amines and mixtures thereof, hindered phenols, phenothiazines, and their derivatives.

The antioxidants are typically used in an amount in the range 1 to 5%.

Antiwear additives include hydrocarbyl phosphate esters, particularly trihydrocarbyl phosphate esters in which the hydrocarbyl radical is an aryl or alkaryl radical or mixture thereof. Particular antiwear additives include tricresyl phosphate, t-butyl phenyl phosphates, trixylenyl phosphate, and mixtures thereof.

The antiwear additives are typically used in an amount in the range 0.5 to 4 wt%, preferably 1 to 3 wt%.

Corrosion inhibitors include but are not limited to various triazols e.g. tolyl triazole, 1,2,4 benzene triazol, 1,2,3 benzene triazol, carboxy benzo-triazole, alkylated benzotriazole and organic diacids, e.g., sebacic acid.

The corrosion inhibitors can be used in an amount in the range 0.02 to 0.5 wt%, preferably 0.05% to 0.25 wt%.

As previously indicated, other additives can also be employed including hydrolytic stabilizers, pour point depressants, anti-foaming agents, viscosity and viscosity index improvers, etc.

Lubricating oil additives are described generally in "Lubricants and Related Products" by Dieter Klamann, Verlag Chemie, Deerfield, Florida, 1984, and also in "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith, 1967, pp. 1-11, the disclosures of which are incorporated herein by reference.

The additive combinations are useful in ester fluids including lubricating oils, particularly those ester fluids useful in high temperature avionic (turbine engine oils) applications. The additive combinations of the present invention exhibit excellent deposit inhibiting performance and improved oxidative stability as measured in the Inclined Panel Deposition Test.

The present invention is further described by reference to the following non-limiting examples.

EXAMPLE 1

This example illustrates the deposit formation performance for the most preferred embodiment of the invention by evaluating fully formulated oils in the Inclined Panel Deposit Test ("IPDT"). The additives tested were blended into a finished turbo oil formulation suitable for applications covered by the MIL-L-23699 specifications by using a constant package of additives and base-stock. The basestock was a technical pentaerithritol ester made with an acid mixture of C₅ to C₁₀ commercially available acids. The additive package contained diaryl amine antioxidants, a commonly used metal passivator containing triaryl phosphates, a corrosion inhibitor consisting of alkylated benzotriazole, and a hydrolytic stabilizer. The total concentration of these other additives was 4.342 gms/100 gms polyol ester base stock.

The IPDT is a bench test consisting of a stainless steel panel electrically heated by means of two heater inserted into holes in the panel body. The test temperature is held at 299°C. The panel temperature is monitored using a recording thermocouple. The panel is inclined at a 4° angle and oil is dropped onto the heated panel near the top, allowing the oil to flow the length of the panel surface, drip from the end of the heated surface and be recycled to the oil reservoir. The oil forms a thin moving film which is in contact with air flowing through the test chamber. Test duration is 24 hours. Deposits formed on the panel are rated on a scale identical to that used for deposits formed in the bearing rig test (FED. Test Method STD. No. 791C, Method 3410.1). Varnish deposits rate from 0 (clean metal) to 5 (heavy varnish). Sludge deposits rate from 6 (light) to 8 (heavy). Carbon deposits rate from 9 (light carbon) to 11 (heavy/thick carbon). Higher ratings (12 to 20) are given to carbon deposits that crinkle or flake away from the metal surface during the test. The total weight of

the deposit formed in 24 hours is also measured. In addition, the final viscosity, measured at 40°C, and Total Acid Number ("TAN"), expressed as mg KOH/100 ml, of the used oil are measured after the test is complete, and used as an evaluation of the oxidation of the oil.

Table 1 illustrates the deposition synergistic effect between a series of DMTD derivatives and triazine compound III, "Triazine", where R₁, R₂, R₃, and R₄ are all dibutylamino and X is piperidino. The DMTD derivatives used were:

Compound A: DMTD compound (I) wherein R' and R" are H

Compound B: DMTD compound (I) wherein R' is butyl and R" is H

Compound C: DMTD compound (I) wherein R' and R" are CH₂-C₆H₆
(bis(s-benzyl))

Compound D: DMTD compound (I) wherein R" are butyl.

Compound E: DMTD compound (I) wherein R' is dodecyl and R" is
CH₂-COOH

The concentration of the triazine is 0.6 gms/100 gms basestock in all cases.

TABLE 1

<u>DMTD Compound</u>	<u>Triazine</u>	<u>DMTD Concentration</u>	<u>Deposit Rating</u>	<u>Deposit Weight</u>
None	None	N/A	4.3	0.24 gms
None	0.6%	None	3.9	0.25 gms
A	None	0.03%	2.8	0.22 gms
A	0.6%	0.03%	2.8	0.05 gms
B	None	0.05%	2.4	0.16 gms
B	0.6%	0.05%	2.0	0.05 gms
C	0.6%	0.05%	2.4	0.13 gms
D	0.6%	0.05%	3.3	0.23 gms
E	None	0.05%	3.8	0.23 gms
E	0.6%	0.05%	3.1	0.26 gms

Table 1 shows that the addition of the triazine has little effect on the deposition performance. The addition of compound A or B without triazine present does improve the deposition rating, and has a small beneficial effect on the deposit weight. However, the addition of triazine to either compound A or B results in an equal or better deposit ratings with much lower total quantity of deposit. For compound A, the result is a 79% reduction in deposit weight for the combination vs. a 8% reduction for compound A alone; for compound B the reduction is 79% for the combination vs. 33% for compound B alone. This illustrates the strong interaction for compounds with at least one uncapped mercapto group.

Compounds C and D show lesser effect, and these materials, with completely "capped" mercapto groups, are less preferred. Compound E does not reduce the amount of deposit.

EXAMPLE 2

Measurement of the oxidative degradation of the oil tested in Example 1 were made by measuring the change in viscosity and acid number, TAN, versus the fresh oil.

Table 2 illustrates the oxidative synergisms for the same compounds in the same test by measuring the percent increase in viscosity and the increase in TAN. The decrease in deposit weight, illustrated in Table 1, might be expected to result in increased Viscosity increase or TAN increase. This is due to solubilization of incipient deposits by the oil resulting in a larger concentration of high molecular weight, partially oxidized molecules. However, Table 2 clearly illustrates that no such effect is observed. Viscosity and TAN changes are uniformly lower for these combinations, especially those with partially or fully uncapped mercapto groups.

TABLE 2

<u>DMTD Compound</u>	<u>Triazine</u>	<u>DMTD Concentration</u>	<u>Viscosity Increase</u>	<u>TAN Increase, mg KOH/L</u>
None	None	N/A	101%	14.2
None	0.6%	None	94%	10.5
A	None	0.03%	18.0%	1.8
A	0.6%	0.03%	6.7%	1.8
B	None	0.05%	3.4%	2.5
B	0.6%	0.05%	1.9%	0.8
C	0.6%	0.05%	40.0%	2.4
D	0.6%	0.05%	25.8%	3.5
E	None	0.05%	169.4%	12.5
E	0.6%	0.05%	87.8%	12.5

Significant improvements in Viscosity and/or TAN increase are observed for combinations of compounds A or B with triazine over any formulation without both compounds present. Compound C and D show lesser performance improvement, while compound E, not part of the present invention, shows no improvement in performance.



WHAT IS CLAIMED IS:

1. A method for enhancing the resistance to deposit formation and improve the oxidative stability of a turbo oil composition comprising a major portion of a synthetic ester based base stock by adding to said turbo oil base stock a minor portion of deposit resisting and oxidation resisting additive comprising a mixture of a non-sulfur containing substituted triazine derivative and 2,5-dimercapto-1,3,4-thiadizole (DMTD), its derivatives or mixtures thereof.

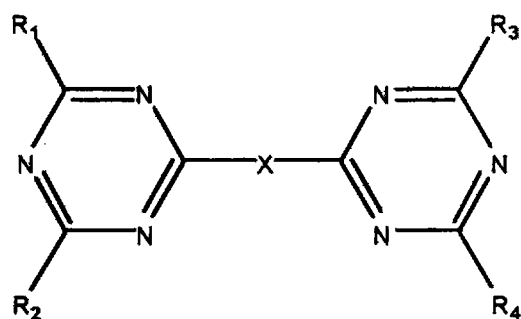
2. The method of claim 1 wherein non-sulfur containing triazine antioxidant is added in an amount in the range 0.1 to 1.2 percent by weight percent, while the 2,5-dimercapto-1,3,4-thiadizole (DMTD) its derivatives or mixtures thereof is used in an amount in the range 50 to 1000 ppm.

3. The method of claim 1 wherein the synthetic polyol ester based base stock is the esterification product of an aliphatic polyol containing 4 to 15 carbon atoms and from 2 to 8 esterifiable hydroxyl groups reacted with a carboxylic acid containing from 4 to 12 carbon atoms.

4. The method of claim 3 wherein the synthetic ester based base stock is the esterification product of technical pentaerythritol and a mixture of C₄ to C₁₂ carboxylic acids.

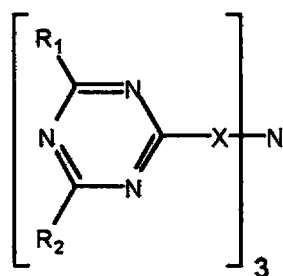
5. The method of claim 1 wherein the non-sulfur containing triazine antioxidant and trithiocyanuric acid are added in a ratio in the range of 2:1 to 100:1.

6. The method of claims 1, 2, 3, 4 or 5 where the substituted triazine is of the formula:



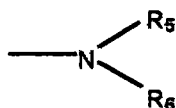
III

or



IIIa

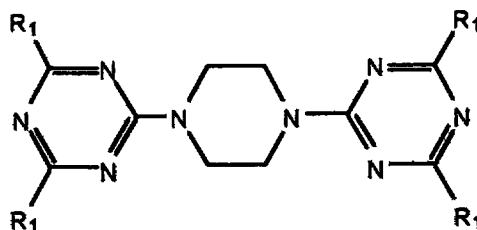
where R_1, R_2, R_3, R_4 are the same or different and are



wherein R_5 and R_6 are the same or different and are selected from the group consisting of C_2 to C_{16} branched or straight chain alkyl, aryl- R_7 where R_7 is branched or straight chain C_2 to C_{16} alkyl, or cyclohexyl- R_7 where R_7 is H or branched or straight chain C_2 to C_{16} alkyl, and mixtures thereof and wherein in formula III X is a bridging group selected from the group consisting of piperidino, hydroquinone, $NH-R_8-NH$ and mixtures thereof where R_8 is C_1 to C_{12} branched or straight chain alkyl, and mixtures thereof and in formula IIIa X is selected from the group consisting of piperidino, hydroquinone, or $NH-R_8$ and mixtures thereof where R_8 is C_1 to C_{12} branched or straight chain alkyl and mixtures thereof.

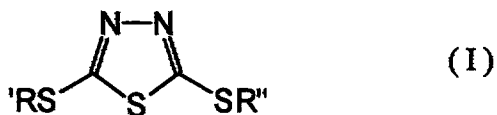


7. The method of claim 6 where the substituted triazine is of the formula:

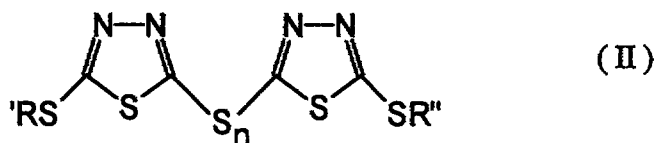


where R₁ is dibutylamino.

8. The method of claims 1, 2, 3, 4, or 5 wherein the DMTD is of the formula:



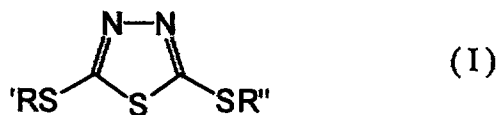
or



where R' and R'' are same or different and are hydrogen, alkyl, cycloalkyl, alkyl-substituted cycloalkyl, aryl, alkylester, alkyl ether wherein R' and R'' in total contain 30 carbons or less and n = 1-2.

9. The method of claim 8 wherein R' or R'' is H.

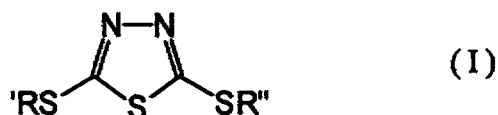
10. The method of claim 6 wherein the DMTD is of the formula:





where R' and R" are same or different and are hydrogen, alkyl, cycloalkyl, alkyl-substituted cycloalkyl, aryl, alkylester, alkyl ether and mixtures thereof wherein R' and R" in total contain 30 carbons or less.

11. The method of claim 7 wherein the DMTD is of the formula:



where R' and R" are same or different and are hydrogen, alkyl, cycloalkyl, alkyl-substituted cycloalkyl, aryl, alkylester, alkyl ether and mixtures thereof wherein R' and R" in total contain 30 carbons or less.

12. The method of claim 10 and 11 wherein in the DMTD of formula (I) R' and R" are H.