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HIGH TEMPERATURE MECHANICAL FLUID COMPOSITIONS

Fred S. Arimoto, Newark, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention is directed to improved antioxidant compositions for use in mechanical fluids at elevated temperatures; and, more particularly, an N-aryl-2-naphthylamine or an acridine in combination with selected polynuclear aromatic hydrocarbons as a stabilizing agent. Mechanical fluids are those fluids adaptable for use as lubricants, heat transfer agents, power transmission agents, hydraulic fluids and the like. The polynuclear aromatic hydrocarbons are selected from the group that has at least three fused rings and a singlet-triplet excitation energy less than 20,000 $cm.^{-1}$ and are represented by such compounds as anthracene, benzanthracene, chrysene, pyrene. The singlet-triplet excitation energy for a number of aromatic hydrocarbons is given in the Journal of the American Chemical Society, vol. 77, page 1949 (1955). This invention also deals with the stabilization of mechanical fluids against the deleterious effects of heat and oxygen at elevated temperatures.

Untreated mechanical fluids, such as the esters and silicone oils, that are adapted for use at 300° F. and above absorb oxygen at these elevated temperatures and undergo undesirable changes. The combination of heat and oxygen, for example, causes the fluids to undergo an increase in viscosity. In some fluids, however, the viscosity may decrease which is also undesirable. These oxidized fluids may become corrosive to metals. This condition limits the kinds of metal that may be used in contact with the fluid and may cause failure or troublesome operation of such metal parts. The deposition of sludge is another condition that arises when these fluids are subjected to thermal and oxidative stresses.

Numerous stabilizing agents have been applied to overcome or to suppress the changes encountered in mechanical fluids at elevated temperatures. Many of the agents have a stabilizing action at mildly elevated temperatures; but above 300° F. and particularly around 500° F., agents that are stabilizers at lower temperatures may lose their effectiveness, actually promote oxidation and become prooxidants. One such agent is phenothiazine. Phenothiazine is commonly used as an antioxidant in synthetic lubricants designed for use at high temperatures in aircraft gas turbines. Its usefulness, however, is limited because at about 400° F., and at higher temperatures, phenothiazine accelerates oxidation thereby promoting the degradation of the lubricant and causing heavy amounts of sludge to form.

It is an object of the present invention to provide novel stabilizing agents that are effective, at elevated temperatures, to retard undesirable changes a mechanical fluid may undergo on exposure to heat and oxygen; the changes retarded include a change in viscosity, the formation and deposition of sludge and the development of corrosive action on metals. It is another object of this invention to inhibit the oxygen absorption of mechanical fluids at

elevated temperatures. It is a further object of this invention to improve the stability of mechanical fluids so that said fluids, when utilized at high temperatures, reflect a minimum change in viscosity, a minimum corroding of metals, and a minimum deposition of sludge. These objects are achieved by treating the mechanical fluid with a small amount of an acridine or an N-aryl-2-naphthylamine in combination with a small amount of a polynuclear hydrocarbon such as anthracene, chrysene, or pyrene; a synergistic effect is achieved in this combination of agents. These and other objects will become apparent in the following description and claims.

More specifically, the present invention is directed to a mechanical fluid for use at 300° F. and above, said fluid containing an antioxidant composition of an N-aryl-2-naphthylamine or an acridine and a polynuclear aromatic hydrocarbon having at least three fused rings and whose singlet-triplet excitation energy is less than 20,000 $cm.^{-1}$.

This invention contemplates a mechanical fluid containing one of the described and claimed novel combinations of antioxidants in an amount within the range of 0.025% to 2.5% by weight of fluid for each component of said combination.

Mechanical fluids suitable for use as lubricants may be the ester or silicone oil type represented by bis(2-ethylhexyl)sebacate, tetrabutyl pyromellitate, tetrakis (1H,1H, ωH-polyfluoroalkyl) pyromellitate (alkyl=C_5 and C_7), pentaerythritol tetrapivalate, and DC–550 silicone oil. The lubricant must be adapted for use at elevated temperatures; that is, it must have a low vapor pressure and be stable enough with the protection that the combinations of stabilizing agents provide to be used at temperatures in the range of 500° F.

The synergistic combinations of the antioxidants of this invention are specific in their effectiveness as illustrated in Table I and are particularly valuable for protecting fluids of the ester and silicone oil types against the damaging effects of heat and oxygen at temperatures from 300° F. and above. These temperatures are commonly encountered in the ester type lubricants used in the bearings of gas turbine engines and may be reached by the ester compounds used as hydraulic fluids. Representative combinations of agents that exhibit significant synergism are acridine and pyrene, anthracene and N-phenyl-2-naphthylamine, and N-phenyl-2-naphthylamine and pyrene. The preferred combination is acridine and pyrene.

To illustrate the improvement of the esters and silicone oils in their resistance to oxygen absorption and to viscosity change and in the reduction of their corrosion of metals at elevated temperatures, the following examples of the marked effect of the combinations of selected stabilizing agents are given. The examples are preceded by a description of the test apparatus and procedure, and part of the test results are presented in tables.

In determining the effect of heat and oxygen at elevated temperatures on mechanical fluids, and, measuring the stabilizing action of antioxidants under these conditions, a 20 mm. glass tube of 25 ml. capacity, rounded on the bottom and sealed at the top with a ground glass joint, was utilized. The glass joint bears a 5 mm. open glass tube that extends almost to the bottom of a 20 mm. tube or oxidation cell; from the glass joint also extends a side outlet tube; this side outlet tube is connected in series

with a U-tube containing anhydrous calcium sulfate as a water-absorbent material, a U-tube containing asbestos flakes impregnated with sodium hydroxide as a carbon dioxide absorbent material, an acetone/solid carbon dioxide trap for condensing volatile oxidation products, a small pump to circulate oxygen in the closed system, and a rotameter to measure the rate of flow of oxygen. A gas burette of oxygen and thermobarometer to compensate for temperature and pressure changes are connected in series with each other and as a side branch to the oxygen absorption system.

To measure the oxidation of a mechanical fluid, the effects of heat and oxygen on the fluid, and the stabilizing effect of an agent or combination of agents, a 10 ml. or 20 ml. sample of fluid, with and without an added agent to be tested, is placed in the oxidation cell and the cell connected to the assembled apparatus through the ground glass joint. The burette is filled with oxygen, and the system temporarily open to the air through a stop-cock is flushed with oxygen. After testing for leaks (by observing if the system will maintain a pressure of 10 to 20 mm. of mercury above that of the atmosphere for five minutes without change) and being sure there are none the oxygen pressure is equalized to that of the atmosphere. The pump is started, and the oxygen flow is set at 25 ml./min. by adjusting the stopcock on the outlet side of the pump. A Woods metal bath at the desired temperature, say 500° F., is raised around the oxidation cell. The oxygen burette is read every five minutes for three hours. The burette is refilled with oxygen as necessary through a stopcock. To measure the viscosity change in a fluid under the test conditions, the material before and after oxidation is permitted to flow through a calibrated modified Ostwald viscosimeter (ASTM procedure D445–46T). To determine the corrosive action of an oxidized fluid at elevated temperatures metal sheet or foil test pieces about one inch square are immersed in the fluid to be oxidized and measured for weight loss after the test.

In the representative examples which follow, the following alkyl and benz substituted acridine compounds as 3-methylacridine, 2,7-dimethylacridine, 2,4,5,7-tetramethylacridine, benz[a]acridine, 10-methylbenz[a]acridine, 8,9-dimethylbenz[a]acridine, 8,9,12-trimethylbenz[a]acridine, benz[c]acridine, 9-methylbenz[c]acridine, and 10,11-dimethylbenz[c]acridine may be substituted for the acridine component to give substantially the same desired results as those achieved with acridine per se.

It is also to be understood that N-aryl-2-naphthylamine, such as N-o-tolyl-2-naphthylamine, N-2-naphthyl-2-naphthylamine and N-9-anthranyl-2-naphthylamine may be substituted for the N-phenyl-2-naphthylamine of the following examples, substantially the same effectiveness being achieved.

The following represent preferred combinations of the antioxidants of the present invention:

N-phenyl-2-naphthylamine with anthracene
N-phenyl-2-naphthylamine with pyrene
N-phenyl-2-naphthylamine with chrysene
Acridine with anthracene
Acridine with chrysene
Acridine with pyrene

The novel antioxidant compositions of the present invention may be prepared and sold in mechanical fluids for use at high temperatures; these novel compositions may also be sold as semi-refined products containing some substantial quantities of the antioxidants. It is to be understood that mixtures of these antioxidants may be prepared and that said mixtures may contain minor amounts of inert material.

Representative examples illustrating the present invention are as follows.

EXAMPLE 1

The effect on the rate of oxygen absorption by bis(2-ethylhexyl) sebacate and on its viscosity increase in three hours at 500° F. in the absence and presence of selected antioxidants and combinations of antioxidants is shown in Table I.

Table I

OXIDATION OF BIS(2-ETHYLHEXYL) SEBACATE

[20 ml. sample at 500° F., oxygen at 25 ml./min.]

No.	Agent Tested	Amt., Percent by Weight	Oxygen Ave. for 1st hr. ml./min.	Absorbed Ave. for 3rd hr. ml./min.	Total Oxygen Absorbed in 3 hrs. ml.	Relative Oxidation Rate		Viscosity Increase in percent measured at ° F.	
						1st hr.	2nd hr.	100	210
1	None		3.17	1.86	456	1	1	22	28
2	Acridine	0.5	2.05	1.36	308	0.65	0.73		
3	Anthracene	0.5	2.29	1.62	395	.75	.87	27	26
4	Chrysene	0.5	3.40	2.48	513	1.07	1.34	17	38
5	N-Phenyl-2-naphthylamine	0.5	2.60	1.68	369	.82	.90	27	27
6	Pyrene	0.5	2.86	2.47	460	.90	1.33	16	28
7	Acridine + anthracene	0.25+0.25	1.37	.71	186	.43	.38	8	11
8a	Acridine + pyrene	0.025+0.025	2.33	1.59	344	.74	.86		
8b	Acridine + pyrene	0.05+0.05	1.00	0.71	188	.31	.38		
8c	Acridine + pyrene	2.5+2.5	2.21	1.45	335	.70	.78		
9	Anthracene + N-phenyl-2-naphthylamine.	0.25+0.25	1.71	1.33	262	.54	.72	11	15
10	Chrysene + N-phenyl-2-naphthylamine.	0.25+0.25	2.04	1.33	298	.64	.71	11	19
11	N-phenyl-2-naphthylamine + pyrene	0.25+0.25	1.69	1.30	292	.53	.70	14	21

The combinations of acridine and anthracene (No. 7), acridine and pyrene (particularly No. 8*b*) anthracene and N-phenyl-2-naphthylamine (No. 9), chrysene and N-phenyl-2-naphthylamine (No. 10), and N-phenyl-2-naphthylamine and pyrene (No. 11) markedly retard the rate of oxidation of bis(2-ethylhexyl) sebacate and definitely reduce its viscosity increase under these oxidizing conditions. Thus these combinations of agents are distinct stabilizers for the ester at the elevated temperature. The same agents used alone (Nos. 2, 3, 4, 5, 6) in an amount equal to that of the total amount of the combination stabilize the ester much less than when used in a proper combination and may actually promote oxidation, chrysene, for example (No. 4).

EXAMPLE 2

The combinations of anthracene and N-phenyl-2-naphthylamine and of N-phenyl-2-napthylamine and pyrene effectively retard the oxidation and viscosity changes of tetrakis(1H,1H,ωH-polyfluoroalkyl) pyromellitate that is subjected to contact with oxygen at elevated temperatures. This polyfluoroalkyl ester has an alkyl group that is a mixture of C_5 and C_7 atom chains. On being oxidized

as described above at 572° F. and at 662° F. the results recorded in Table II were obtained.

Table II

OXIDATION OF TETRAKIS (1H, ωH, kH-POLYFLUOROALKYL) PYROMELLITATE

[10 ml. ester]

A. TEMPERATURE, 572° F.

Agent Tested	Amt., percent by Weight	Oxygen Absorbed			Viscosity Change in percent Measured at ° F.	
		Ave. for 1st hr., ml./min.	Ave. for 2nd hr., ml./min.	Total in 3 hrs., ml.	100	210
None		2.32	0.63	170	−31	−28
Anthracene and N-phenyl-2-naphthylamine	0.25+.25	0.05	.08	9	−7	−0
N-Phenyl-2-naphthylamine and pyrene	0.25+0.25	0.07	.04	8	−7	+1
B. TEMPERATURE, 662° F.						
None		2.70	.50	186	+70	+25
N-Phenyl-2-naphthylamine and pyrene	0.25+0.25	.47	.17	47		−5

EXAMPLE 3

A combination of acridine and pyrene retards the increase in viscosity and the corrosion of metals in tetrabutyl pyromellitate through which air is bubbled at 500° F. This oxidation corrosion test is a standard procedure (Federal Test Method Standard No. 791, Method 5308.4) used for qualifying lubricants under MIL–L–9236 specification. The test results are summarized in Table III.

Table III

OXIDATION OF TETRABUTYL PYROMELLITATE

[100 ml. sample at 500° F., air flow at 83 ml./min.]

	Control (No added agent)	Ester plus 0.25% Acridine and 0.25% pyrene
Viscosity, percent increase measured at 210° F.	39.2	7.4
Metal Strip Weight loss (mg./cm.²):		
Aluminum	0.03	+0.05
Copper	10.07	1.14
Magnesium	0.26	+0.07
Silver	0.06	0.00
Steel	0.04	+0.04
Titanium	0.05	+0.04

EXAMPLE 4

Anthracene (0.25 part) and N-phenyl-2-naphthylamine (0.25 part) added to 100 parts of pentaerythritol tetrapivalate so retards oxidation at 500° F. when oxygen is bubbled through a 10 ml. sample of the ester in the apparatus and by the procedure described for the tests with bis(2-ethylhexyl) sebacate summarized in Table I that only 8 ml. of oxygen are absorbed in three hours whereas the untreated ester absorbs 87 ml. of oxygen in the same time. The viscosity at 100° F. of the treated ester increases from 298 centistokes before oxidation to only 312 centipoises or 5% after the oxidation while the viscosity of the untreated control sample increases to 410 centistokes or 38%.

EXAMPLE 5

The effect of acridine and pyrene in combination and of anthracene and N-phenyl-2-naphthylamine used together in a methyl phenyl silicone (DC–550 silicone oil) is marked in retarding oxidation at 572° F. and in suppressing an increase in viscosity in the oil. The results of oxidizing the silicone oil as the esterlubes have been oxidized with recirculated oxygen are presented in Table IV.

Table IV

OXIDATION OF DC–550 SILICONE OIL

[20 ml. sample at 572°F., oxygen at 25 ml./min.]

Agent Tested	Amount Percent by Weight	Oxygen Absorbed, ml. in 3 hours	Viscosity increase in percent measured at °F.	
			100	210
None		97.4	21	15
Anthracene and N-phenyl-2-naphthylamine	0.25+0.25	29.4	5.7	3.1
Acridine and pyrene	0.25+0.25	15.6	4.5	2.7

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be underestood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

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

1. A high temperature mechanical fluid selected from the group consisting of esters and silicone oils, said fluid containing an antioxidant composition of a component selected from the group consisting of an N - aryl-2-naphthylamine and an acridine, in combination with a polynuclear aromatic hydrocarbon component having at least three fused rings said polynuclear aromatic hydrocarbon being selected from the group consisting of anthracene, benzanthracene, chrysene and pyrene, the singlet-triplet excitation energy of said hydrocarbon being less than 20,000 $cm.^{-1}$, each of said antioxidant components being present in an amount within the range of 0.025% to 2.5% by weight of said mechanical fluid.

2. A high temperature mechanical fluid according to claim 1 wherein the antioxidant composition is a combination of acridine and pyrene.

3. An antioxidant composition for high temperature mechanical fluids selected from the group consisting of esters and silicone oils, said composition consisting of a component selected from the group consisting of an N-aryl-2-naphthylamine and an acridine, together with a polynuclear aromatic hydrocarbon component having at least three fused rings, said polynuclear aromatic

hydrocarbon being selected from the group consisting of anthracene, benzanthracene, chrysene and pyrene, the singlet-triplet excitation energy of said hydrocarbon being less than 20,000 $c^{m.-1}$, the proportion of said components being in equal parts by weight and each of said components being present in an amount to achieve a concentration in said mechanical fluid within the range of 0.025% to 2.5% by weight of said fluid.

4. An antioxidant composition according to claim 3 wherein said composition is a combination of acridine and pyrene.

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