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ANTIOXIDANT COMPOSITION AND SYNTHETIC LUBRICANT CONTAINING IT

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This invention relates to ester type synthetic lubricants and to the problem of protecting them from oxidative degradation.

Synthetic lubricants of the ester type have replaced petroleum oils in many lubricant and hydraulic fluid applications where severe service conditions are encountered. As an example, esters such as bis(2-ethylhexyl)sebacate are used almost universally as lubricants in aircraft turbine engines of the pure jet and prop-jet types. However, under such severe service conditions, these organic esters as a class are very susceptible to oxidation. Consequently, in formulating satisfactory jet engine lube oils from esters and the like, measures must be taken to protect these esters from oxidative attack under these severe service conditions.

Phenothiazine has been one of the most used antioxidants for ester type synthetic lubricants. It has been reasonably satisfactory for moderately high jet engine temperatures. However, as is well-known, phenothiazine is a "dirty" antioxidant, causing the formation of insoluble sludges during lubricant use. In addition to such sludging characteristics, phenothiazine does not appear to stabilize ester lubricants satisfactorily at the higher temperatures for which current military and civil jet engines are being designed.

A problem, therefore, to which this invention provides a solution is how to minimize, if not eliminate, the sludging characteristics of phenothiazine under the more severe service conditions and particularly higher temperatures, as well as to increase the stabilizing action of the phenothiazine at these higher temperatures.

This invention is based upon the discovery that small amounts of acidic phosphorus compounds greatly improve the antioxidant properties of arylamine type antioxidants and particularly phenothiazine in ester lube oils for aircraft jet engines. The acidic phosphorus compounds have been found to retard the sludging or "dirtiness" caused by the arylamine antioxidants and to increase the antioxidant action or stabilizing action of the arylamine antioxidants.

In summary, this invention comprises an antioxidant composition particularly useful for ester type synthetic lubricants. In addition, this invention broadly comprises an ester type synthetic lubricant containing the antioxidant composition at an effective or protective concentration.

The antioxidant composition of this invention comprises a mixture consisting essentially of an arylamine antioxidant portion and at a minor concentration relative to the arylamine antioxidant portion an acidic phosphorus portion.

The arylamine antioxidant portion of the composition consists essentially of at least one arylamine antioxidant. Examples of an arylamine antioxidant include phenothiazines such as phenothiazine, phenothiazine derivatives containing substituents on the nitrogen atom and phenothiazine derivatives containing substituents on the rings, alkylated diphenylamines, N-phenylnaphthylamines and dinaphthylamines. Preferred arylamine antioxidants include N-alkylphenothiazines wherein the N-alkyl group has 1-18 carbon atoms, N-phenyl-1-naphthylamine and p,p'-dialkyl diphenylamines such as p,p'-dioctyldiphenyl-

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amine, wherein the p and p'-alkyl groups each have 1-18 carbon atoms. In preferred embodiments of this invention the arylamine antioxidant portion consists essentially of a mixture of an N-alkylphenothiazine and a p,p'-dialkyldiphenylamine. Typical examples of such a mixture include:

N-ethylphenothiazine and p,p'-dioctyldiphenylamine
N-butylphenothiazine and dinonyldiphenylamine
N-octylphenothiazine and p,p'-dibutyldiphenylamine
N-dodecylphenothiazine and p,p'-dioctyldiphenylamine
N-ethylphenothiazine and N-phenyl-1-naphthylamine
N-acetylphenothiazine and p,p'-dioctyldiphenylamine
N-methylphenothiazine and N-phenyl-2-naphthylamine
N-decylphenothiazine and diphenylamine
N-ethylphenothiazine and di-1-naphthylamine

The weight ratio of the N-alkylphenothiazine to the p,p'-dialkyldiphenylamine is generally in a range from about 1:3 to about 3:1 and preferably in a range from about 2:3 to about 3:2.

The acidic phosphorus portion of the antioxidant composition of this invention consists essentially of at least one acidic phosphorus compound. This is a compound having at least one acid (OH) group attached to a phosphorus atom. Such a compound is present in phosphoric acid, phosphorous acid and organic partial esters of these acids. The organic partial esters of these acids are preferred since they are more soluble in the esters normally employed as synthetic lubricants, and are less extractable therefrom by aqueous solutions. The organic partial esters of phosphoric acid include alkyl dihydrogen phosphates, dialkyl hydrogen phosphates, aryl dihydrogen phosphates, diaryl hydrogen phosphates, alkylaryl dihydrogen phosphates and di(alkylaryl)hydrogen phosphates. It is preferred that the alkyl groups in these compounds that have such contain 1-8 carbon atoms. The organic partial esters of phosphorous acid include alkyl dihydrogen phosphites, dialkyl hydrogen phosphites, aryl dihydrogen phosphites, diaryl hydrogen phosphites, alkylaryl dihydrogen phosphites and di(alkylaryl)hydrogen phosphites. Here, too, it is preferred that the alkyl groups in these compounds that have such contain 1-8 carbon atoms. Under the concepts of this invention the acidic phosphorus portion of the antioxidant composition of the invention can consist essentially of a mixture of acidic phosphorus compounds. Generally, the acidic phosphorus esters are obtained commercially as mixtures of the monoalkyl and dialkyl derivatives and are referred to as alkyl acid phosphates and alkyl acid phosphites. These mixtures are within the concepts of this invention. Preferred, specific, acidic phosphorus compounds include ethyl acid phosphate, butyl acid phosphate, methyl acid phosphate and phosphorous acid.

Concentration of the arylamine antioxidant portion of the mixture which characterizes the antioxidant composition of this invention is generally greater than the concentration of the acidic phosphorus portion of the mixture. Usually, concentration of the arylamine antioxidant portion is broadly in a range from about 95.3 to about 99.95 by weight of the mixture and preferably in a range from about 97.6 to about 99.75. Concentration of the acidic phosphorus portion of the mixture usually is broadly in a range from about 0.05 to about 4.7% by weight of the mixture and preferably in a range from about 0.25 to about 2.4% by weight of the mixture.

The antioxidant composition is prepared by admixing the components thereof until a uniform blend is obtained.

The synthetic lubricant of this invention consists essentially of an organic ester base stock and at a protec-

tive concentration the antioxidant composition of this invention.

The organic ester base stock consists essentially of at least one organic ester which is an oil at 20° C. Such an ester is provided by various diesters of dibasic acids and alcohols, diesters of monobasic acids and glycols, triesters of monobasic acids and trihydric alcohols such as trimethylolethane, trimethylolpropane and the like, pentaerythritol tetraesters, and polyesters such as those obtained from a dibasic acid and a glycol and chain terminated with either an alcohol or a monobasic acid. Typical organic esters include:

2-butyl-2-ethyl-1,3-propanediol dipelargonate
2-ethyl-2-isobutyl-1,3-propanediol diundecanoate
2,2-diethyl-1,3-propanediol dipelargonate
Bis(2,2,4-trimethylpentyl)azelaate
Bis(2,2,4-trimethylpentyl)undecanedioate
Bis(2-methyl-2-norcamphanylmethyl)sebacate
1,1-cyclopentanedimethanol dipelargonate
Trimethylolpropane triheptanoate
Pentaerythritol tetrahexanoate
Bis(2-ethylhexyl)sebacate
Esters of alcohols and oleic acid dimers and trimers
Polyester of azelaic acid, neopentyl glycol and 2,2,4-trimethylpentanol at a mole ratio of 1:1:0.25
Polyester of azelaic acid, 2-butyl-2-ethyl-1,3-propanediol and octanoic acid at a mole ratio of 1:1:0.25

Concentration of the antioxidant composition of this invention in the synthetic lubricant in general depends upon the ester base stock and on the degree of stability desired. However, in general, a concentration of the antioxidant composition in a range from about 0.1005 to about 5.2% by weight of the ester base stock and preferably in a range from about 0.201 to about 4.05% by weight of the ester base stock gives satisfactory results. At these concentrations, the concentration of the arylamine antioxidant portion of the antioxidant composition is in a general range from about 0.1 to about 5% by weight of the ester base stock and preferably in a range from about 0.2 to about 4% by weight of the ester base stock. Similarly, at these concentrations, the acidic phosphorus portion of the antioxidant composition is present at a concentration in a general range from about 0.0005 to about 0.2% by weight of the ester base stock and preferably in a range from about 0.001 to about 0.05% by weight of the ester base stock.

Besides the ester base stock and antioxidant composition, the synthetic lubricant of this invention can also comprise other additives such as lubricity improvers, anticorrosion agents, metal deactivators, detergents, dyes and phenolic antioxidants.

The synthetic lubricant of this invention is prepared merely by admixing the components thereof until a uniform blend, usually in the form of a solution, is obtained. In admixing the components of the synthetic lubricant, the antioxidant composition can be added as such to the ester base stock or the components of the antioxidant composition can be individually added to the ester base stock whereby the antioxidant composition is formed in the ester base stock.

The synthetic lubricant of this invention is suitable for a variety of severe service uses. Indeed specific embodiments thereof satisfy military and civil jet engine specifications such as MIL-L-7808D, MIL-L-25,336, MIL-L-9236B, MIL-L-27,502, DERD 2487 and others. In addition the synthetic lubricant has utility under less severe service conditions as a hydraulic fluid, industrial lubricant, coolant fluid and automotive lubricant.

This invention is further illustrated by the following examples of various aspects thereof, including preferred specific embodiments of the invention. This invention is not limited to these specific embodiments unless otherwise indicated.

Specific embodiments of the antioxidant composition of this invention are formulated as follows:

EXAMPLE 1

Components:	Parts by weight
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	0.1

EXAMPLE 2

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	0.5

EXAMPLE 3

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	0.75

EXAMPLE 4

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	1

EXAMPLE 5

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	2

EXAMPLE 6

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	10

EXAMPLE 7

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Dodecyl acid phosphate	1

EXAMPLE 8

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
2,2 - dimethyl - 1,3 - propanediol - cyclic - hydrogen-phosphate	0.6

EXAMPLE 9

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
o-Phosphoric acid	0.36

EXAMPLE 10

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
o-Phosphoric acid	0.42

EXAMPLE 11

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
2,2 - dimethyl - 1,3 - propanediol - cyclic - hydrogen-phosphite	1

EXAMPLE 12

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Diethyl hydrogen phosphite	0.44

EXAMPLE 13

Components:	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Bis(2-ethylhexyl) hydrogen phosphite	1

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EXAMPLE 14

Components:	Parts by weight	
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	1	5

EXAMPLE 15

Components:		
N-ethylphenothiazine	100	
N-phenyl-1-naphthylamine	100	
Ethyl acid phosphate	0.5	10

EXAMPLE 16

Components:		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Butyl acid phosphate	1.3	15

EXAMPLE 17

Components:		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Diphenyl hydrogen phosphate	1.2	20

EXAMPLE 18

Components:		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Methyl acid phosphate	0.6	25

Each one of the antioxidant compositions of the foregoing specific formulations are prepared merely by admixing the components at room temperature until a uniform blend is obtained.

Specific embodiments of the synthetic lubricant of this invention are formulated as follows.

EXAMPLE 19

Components:	Parts by weight	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000	
Antioxidant composition—		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	0.1	35

EXAMPLE 20

Components:		
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000	
Antioxidant composition—		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	0.5	45

EXAMPLE 21

Components:		
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000	
Antioxidant composition—		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	0.75	50

EXAMPLE 22

Components:		
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000	
Antioxidant composition—		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	1	60

EXAMPLE 23

Components:		
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000	
Antioxidant composition—		
N-ethylphenothiazine	100	
p,p'-Diocetyl-diphenylamine	100	
Ethyl acid phosphate	2	75

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EXAMPLE 24

Components:	Parts by weight
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Ethyl acid phosphate	10

EXAMPLE 25

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Dodecyl acid phosphate	1

EXAMPLE 26

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
2,2-dimethyl-1,3-propanediol-cyclic hydrogen-phosphate	0.6

EXAMPLE 27

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
o-Phosphoric acid	0.36

EXAMPLE 28

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
o-Phosphoric acid	0.42

EXAMPLE 29

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
2,2-dimethyl-1,3-propanediol-cyclic hydrogen-phosphite	1

EXAMPLE 30

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
Samples 6-15 in Table I, it will be noted, have the anti-Diethyl hydrogen phosphite	0.44

EXAMPLE 31

Components:	
Ester base stock—2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Diocetyl-diphenylamine	100
Bis(2-ethylhexyl)hydrogen phosphite	1

EXAMPLE 32

Components:	Parts by weight
Ester base stock—2 - butyl - 2 - ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	5
N-dodecylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Ethyl acid phosphate	1

EXAMPLE 33

Components:	Parts by weight
Ester base stock—2 - butyl - 2 - ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	15
N-ethylphenothiazine	100
N-phenyl-1-naphthylamine	100
Ethyl acid phosphate	0.5

EXAMPLE 34

Components:	Parts by weight
Ester base stock — 2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	20
N-ethylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Butyl acid phosphate	1.3

EXAMPLE 35

Components:	Parts by weight
Ester base stock — 2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	30
N-ethylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Diphenyl hydrogen phosphate	1.2

EXAMPLE 36

Components:	Parts by weight
Ester base stock — 2-butyl-2-ethyl-1,3-propanediol dipelargonate	10,000
Antioxidant composition—	40
N-ethylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Methyl acid phosphate	0.6

EXAMPLE 37

Components:	Parts by weight
Ester base stock—Bis(2,2,4-trimethylpentyl) azelate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Ethyl acid phosphate	1

EXAMPLE 38

Components:	Parts by weight
Ester base stock—Trimethylolpropane triheptanoate	10,000
Antioxidant composition—	
N-ethylphenothiazine	100
p,p'-Dioctyldiphenylamine	100
Ethyl acid phosphate	1

The synthetic lubricant compositions of the foregoing formulations are prepared merely by admixing the various components specified in the formulations. Such mixing is preferably undertaken at room temperature and is continued until the components of the antioxidant composition are dissolved in the ester base stock.

The effectiveness of the antioxidant composition of this invention and the stability of the synthetic lubricant of this invention are demonstrated by the following test data obtained in actual tests on samples of synthetic lubricants formulated as indicated in the following tables. The tests and measurements employed in the testing are as follows.

AF oxidation test

This test, which indicates the oxidation stability of the synthetic lubricant at high temperatures, is described in a paper entitled "Materials for High Temperature Jet Engine Lubricants" (H. E. Adams) in W.A.D.C. Technical Report 59-244 (Air Force, 1959). The test conditions employed in this test are selected to simulate high temperature jet engine and bearing rig operation conditions.

In this test a 250 milliliter sample of the lubricant is heated at 425° F. in a Pyrex test tube while 96 liters of air per hour are blown through it. A freshly polished metal panel is immersed in the lubricant. The test tube is capped with a Pyrex fitting which allows volatile products to escape from the tube. The lubricant in the tube is

TABLE I

Sample No.	Additives				Viscosity acid No. at—		Sludge rating (hours)					
	Arylamines	Cone. in percent by wt. of ester base stock	Acidic phosphorus compound	Cone. in percent by wt. of ester base stock	120 hrs.	120 hrs.	20	40	60	80	100	120
1.....	None		None		104.7 (at 20 hrs.)	12.4 (at 20 hrs.)	0					
2.....	N-ethylphenothiazine	2	do		23.8 (at 60 hrs.)	5.26 (at 60 hrs.)	8	10	10			
3.....	p,p'-Dioctyldiphenylamine	2	do		116.5 (at 20 hrs.)	13.63 (at 20 hrs.)	2					
4.....	N-ethylphenothiazine	1	do		22.2	5.65	0	1	2	6	8	9
5.....	p,p'-Dioctyldiphenylamine	1			30.98 (at 20 hrs.)	17.14 (at 20 hrs.)	0					
6.....	None		Ethyl acid phosphate	0.0075								
7.....	N-ethylphenothiazine	1	do	0.001	22.3	3.64	0	0	1	2	8	8
8.....	p,p'-Dioctyldiphenylamine	1	do	0.005	20.6	3.07	0	0	0	0	0	2
9.....	N-ethylphenothiazine	1	do	0.02	20.9	2.78	0	0	0	1	2	3
10.....	p,p'-Dioctyldiphenylamine	1	do	0.1	22.3	3.07	1	1	1	4	4	5
11.....	N-ethylphenothiazine	1	Dodecylacid phosphate	0.01	21.2	3.01	0	1	1	2	3	3
12.....	p,p'-Dioctyldiphenylamine	1	2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate	0.006	22.5	4.23	1	1	2	3	3	4
13.....	N-ethylphenothiazine	1	o-Phosphoric acid	0.0036	20.8	3.20	0	0	0	1	1	1
14.....	p,p'-Dioctyldiphenylamine	1	do	0.0042	22.5	3.27	1	1	1	2	5	4
15.....	N-ethylphenothiazine	1	Diethyl hydrogen phosphite	0.0044			0	0	0	4		
16.....	p,p'-Dioctyldiphenylamine	1	Bis(2-ethylhexyl) hydrogen phosphite	0.01	22.0	3.85	0	0	0	2	3	4

heated in 20 hour cycles and at the end of each cycle the tube is cooled, a 10 milliliter sample of the lubricant is withdrawn for analysis and the lubricant lost by evaporation is replaced with fresh lubricant. Ordinarily the test is conducted for 6 cycles or 120 hours. The 10 milliliter samples are analyzed for viscosity in centistokes at 100° F. (ASTM Method D445), acid number (in milligrams of KOH per gram) (ASTM Method D974) sludge content. Sludge content is determined by filtering a 2 milliliter sample of the lubricant through a Whatman No. 2 filter paper (4.25 centimeters), washing the paper with 25 milliliters of Stoddard solvent, drying the paper and then rating the sludge deposit on the paper according to a scale from 0 to 10, 0 being equivalent to clean and 10 designating heavy deposit.

In the first series of tests the ester base stock in each sample consisted essentially of 2-butyl-2-ethyl-1,3-propanediol dipelargonate and was characterized by an acid number (milligrams of KOH per gram) of 0.03, a viscosity at -65° F. of 15,084 centistokes, a viscosity at 100° F. of 14.32 centistokes and a viscosity at 210° F. of 3.33 centistokes, an open cup flash point of 443° F. and a pour point of less than -70° F. The test samples containing additives were prepared from this ester base stock and the specific additives at specific concentrations indicated in the preceding Table I. These test samples were prepared merely by admixing the additives into the ester base stock until in each case a uniform blend was obtained. The metal panels employed in these particular tests were made of steel and each had the dimensions: 1 inch by 1 inch by $\frac{1}{32}$ inch. The test results and other test conditions in this first series of tests are set out in the preceding Table I.

Samples 6-15 in Table I, it will be noted, have the antioxidant compositions of Examples 1-2, 5-10 and 12-13, and correspond in formulation to the specific synthetic lubricants of Examples 19-20, 23-28 and 30-31.

In the case of Samples 1, 3 and 5, the AF oxidation test procedure was stopped after 20 hours due to the obviously rapid oxidation of the samples, and viscosity and acid number measurements were then made on these samples. In the case of sample 2, the AF oxidation test procedure was terminated after 60 hours, because of the highly ox-

dized condition of the sample, and viscosity and acid number measurements were then made on the sample. All other samples (4 and 6-15), were subjected to the AF oxidation test for the full 120 hours.

A comparison of the test data of Sample 6 with the test data of Samples 1-5 demonstrates the need for an effective antioxidant composition in the ester base stock and the fact that the antioxidant composition in Sample 6 is effective. Comparison of the data of Samples 6-15 with the data of Sample 4 reveals the dramatic effect of various acidic phosphorus compounds on the antioxidant activity of the arylamine antioxidant mixture of Sample 4, especially in regard to reduction in sludging tendency.

In the next test series summarized in the following Table II, test samples of synthetic lubricants were prepared from different ester base stocks and with various arylamine antioxidants and ethyl acid phosphate. In this series of tests, the ester base stock identified in Table II as BEPD consisted essentially of 2-butyl-2-ethyl-1,3-propanediol dipelargonate and had an acid number (milligrams of KOH per gram) of 0.03, a viscosity at -65° F. of 15,084 centistokes, a viscosity at 100° F. of 14.32 centistokes, a viscosity at 210° F. of 3.33 centistokes, an open cup flash point of 443° F. and a pour point of less than -70° F. The ester base stock identified in Table II as TMPZ consisted essentially of bis(2,2,4-trimethylpentyl) azelate and had an acid number (milligrams of KOH per gram) of 0.06, a viscosity at -65° F. of 8,940 centistokes, a viscosity at 100° F. of 13.14 centistokes, a viscosity at 210° F. of 3.45 centistokes, an open cup flash point of 425° F. and a pour point less than -80° F. The ester base stock identified in Table II as TMPTH consisted essentially of trimethylolpropane triheptanoate and was characterized by an acid number (milligrams of KOH per gram) of 0.07, a viscosity at -65° F. of 17,911 centistokes, a viscosity at 100° F. of 16.09 centistokes, a viscosity at 210° F. of 3.66 centistokes, an open cup flash point of 450° F., and a pour point of less than -65° F. The test samples were prepared by admixing the components thereof until solutions were formed. The metal panels employed in these particular tests were made of steel and each had the dimensions: 1 inch by 1 inch by $\frac{1}{32}$ inch. The test results and test sample formulations are set forth in the following Table II.

TABLE II

Sample No.	Sample composition					Test results							
	Ester base stock	Arylamines	Conc. in percent by wt. of ester base stock	Acidic phosphorus compound	Conc. in percent by wt. of ester base stock	Property	Hours						
							0	20	40	60	80	100	120
1-----	BEPD	N-dodecylphenothiazine p,p'-dioctyldiphenylamine	1 1	None	0.01	Viscosity	15.03	17.95	19.64	21.63	23.63	26.48	31.91
						Acid No.	0.05	2.20	3.68	3.46	3.27	4.75	5.36
						Sludge rating.	0	0	0	1	2	2	4
2-----	BEPD	N-dodecylphenothiazine p,p'-dioctyldiphenylamine	1 1	Ethyl acid phosphate.	0.01	Viscosity	15.03	16.44	17.29	18.36	19.72	20.96	22.48
						Acid No.	0.14	0.96	1.37	1.37	2.08	4.09	2.77
						Sludge rating.	0	0	0	0	1	1	2
3-----	BEPD	N-ethylphenothiazine N-phenyl-1-naphthylamine	1 1	None	0.005	Viscosity	15.03	16.17	18.77	35.23	-----	-----	-----
						Acid No.	0.04	1.00	3.44	9.60	-----	-----	-----
						Sludge rating.	0	6	7	7	-----	-----	-----
4-----	BEPD	N-ethylphenothiazine N-phenyl-1-naphthylamine	1 1	Ethyl acid phosphate.	0.005	Viscosity	15.03	15.81	20.16	49.20	-----	-----	-----
						Acid No.	0.10	0.72	4.42	12.53	-----	-----	-----
						Sludge rating.	0	2	3	6	-----	-----	-----
5-----	TMPZ	N-ethylphenothiazine p,p'-dioctyldiphenylamine	1 1	None	0.01	Viscosity	13.58	15.30	16.38	17.84	19.42	21.61	23.47
						Acid No.	0.15	1.69	2.77	2.64	3.16	3.70	3.66
						Sludge rating.	0	0	2	4	6	8	8
6-----	TMPZ	N-ethylphenothiazine p,p'-dioctyldiphenylamine	1 1	Ethyl acid phosphate.	0.01	Viscosity	13.58	15.07	16.14	17.39	19.30	20.16	22.68
						Acid No.	0.43	0.96	1.99	2.05	3.10	3.19	4.12
						Sludge rating.	0	0	0	1	3	3	3
7-----	TMPTH	N-ethylphenothiazine p,p'-dioctyldiphenylamine	1 1	None	0.01	Viscosity	16.62	20.19	22.40	24.81	28.07	32.09	38.30
						Acid No.	0.03	1.27	1.98	2.55	3.91	3.95	5.52
						Sludge rating.	0	0	0	1	2	2	2
8-----	TMPTH	N-ethylphenothiazine p,p'-dioctyldiphenylamine	1 1	Ethyl acid phosphate.	0.01	Viscosity	16.62	19.50	20.28	22.85	24.65	26.42	29.38
						Acid No.	0.23	0.95	1.51	2.09	2.91	2.87	3.17
						Sludge rating.	0	0	0	0	1	1	1

Sample 2 in Table II has the specific antioxidant composition of Example 14 and corresponds in formulation to the specific synthetic lubricant of Example 32. Sample 4 in Table II has the specific antioxidant composition of Example 15 and corresponds in formulation to the specific synthetic lubricant of Example 33. Samples 6 and 8 have the specific antioxidant composition of Example 4 and correspond in formulation to the specific synthetic lubricants of Examples 37 and 38, respectively.

These data of Table II demonstrate the outstanding effectiveness of the various specific embodiments of the antioxidant composition of this invention in protecting several different ester base stocks from oxidative attack, and particularly in reducing sludging. In addition, these data demonstrate the outstanding stability of a number of specific embodiments of the synthetic lubricant of this invention.

In the next series of tests which are summarized in the following Table III the ester base stock that was used consisted essentially of 2-butyl-2-ethyl-1,3-propanediol dipelargonate and was characterized by an acid number (milligrams of KOH per gram) of 0.03, a viscosity at -65° F. of 15,084 centistokes, a viscosity at 100° F. of 14.32 centistokes, a viscosity at 210° F. of 3.33 centistokes, an open cup flash point of 443° F. and a pour point of less than -70° F. To test samples of this stock were added N-ethylphenothiazine and p,p'-dioclyldiphenylamine, the concentration of each one of these arylamines in the ester base stock being 1% by weight of the ester base stock. Where indicated in the following Table III, specific acidic phosphorus compounds were added to various ones of the test samples. In each case the additives and ester base stock were admixed until a solution was formed. In the stability testing of these test samples, the degree of metal to lubricant contact was increased by replacing the smaller metal panels with larger metal panels (1½ inches by 6 inches by ⅛ inch) and by using both steel and aluminum panels except where otherwise indicated. Formulations of the various test samples and test results are set out in the following Table III.

TABLE III

Sample No.	Acidic phosphorus compound	Conc. in percent by wt. of ester base stock	Metal panels used	Property	Hours						
					0	20	40	60	80	100	120
1.	None		Steel only	Viscosity..... Acid No..... Sludge rating....	15.03 0.04 0	23.03 5.55 1	31.13 9.06 4	42.96 17.97 6	-----	-----	-----
2.	None		Steel plus aluminum	Viscosity..... Acid No..... Sludge rating....	15.03 0.04 0	24.80 6.55 3	37.59 9.65 3	56.36 10.49 6	95.72 10.71 8	-----	-----
3.	Ethyl acid phosphate	0.0075	do.	Viscosity..... Acid No..... Sludge rating....	15.03 0.11 0	16.20 0.69 1	17.05 1.16 0	18.06 1.38 0	19.16 1.84 1	20.35 3.38 1	21.72 3.12 1
4.	Butyl acid phosphate	0.013	do.	Viscosity..... Acid No..... Sludge rating....	15.03 0.12 0	16.47 2.46 2	17.21 1.75 2	18.44 1.96 2	19.59 1.53 2	21.01 2	22.60 3.19 2
5.	{2,2-dimethyl-1,3-propanediol- cyclic-hydrogen-phosphite.	0.01	do.	Viscosity..... Acid No..... Sludge rating....	15.03 0.07 0	16.28 3.15 0	17.15 1.63 0	18.25 2.20 0	19.86 3.68 1	21.06 4.52 4	22.73 4.02 5
6.	Diphenyl hydrogen phosphate	0.012	do.	Viscosity..... Acid No..... Sludge rating....	14.91 0.21 0	16.17 1.26 1	17.03 1.64 2	18.11 1.89 2	19.01 2.57 3	20.05 5	21.47 3.27 6
7.	Methyl acid phosphate	0.006	do.	Viscosity..... Acid No..... Sludge rating....	14.91 0.14 0	16.17 1.38 0	17.08 2.10 0	17.73 2.46 0	18.41 2.15 0	19.41 3.27 0	20.95 3.40 2

Sample 3 of Table III, it will be observed, had the antioxidant composition of Example 3 and corresponded in formulation to the specific synthetic lubricant of Example 21. Sample 4 contained the antioxidant composition of Example 16 and corresponded in formulation to the specific synthetic lubricant of Example 34. Sample 5 had the antioxidant composition of Example 11 and corresponded in formulation to the specific synthetic lubricant of Example 29. Samples 6 and 7 contained the anti-

oxidant compositions of Examples 17 and 18, respectively, and corresponded in formulation to the specific synthetic lubricants of Examples 35 and 36, respectively.

These data of Table III dramatically illustrate the beneficial effect of acidic phosphorus compounds on arylamine antioxidants in stabilizing synthetic lubricants of the ester type. These data show that acidic phosphorus compounds substantially reduce sludging of synthetic lubricants of the ester type, when containing arylamine antioxidants.

Thus, there is provided an antioxidant composition which is particularly useful for synthetic lubricants of the ester type, which are intended for severe service use. Moreover, there is provided a synthetic lubricant which has a high degree of protection relative to oxidative degradation, particularly under severe service conditions.

Other features, advantages and specific embodiments of this invention will be apparent to those in the exercise of ordinary skill in the art after reading the foregoing disclosure. In this connection, while this invention has been described in considerable detail relative to specific embodiments thereof, variations and modifications of these specific embodiments can be effected within the spirit and scope of the invention as disclosed and claimed.

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

1. An antioxidant composition comprising a mixture consisting essentially of (1) an arylamine antioxidant portion consisting essentially of (a) N-alkylphenothiazine wherein the N-alkyl group has 1-18 carbon atoms and (b) p,p'-dialkyldiphenylamine wherein the p and p'-alkyl groups each have 1-18 carbon atoms, the weight ratio of the N-alkyl-phenothiazine to the p,p'-dialkyldiphenylamine being in a range from about 1:3 to about 3:1, and (2) an acidic phosphorus portion consisting essentially of at least one acidic phosphorus compound selected from the group consisting of an alkyl acid phosphate wherein the alkyl group contains from 1 to 10 carbon atoms, o-phosphoric acid, diphenyl hydrogen phosphate, diethyl

hydrogen phosphite, bis(2-ethylhexyl)hydrogen phosphite and 2,2-dimethyl-1,3-propanediol-cyclic-hydrogen-phosphite, the concentration of said arylamine antioxidant portion being in a range from about 95.3 to about 99.95% by weight of said mixture and the concentration of said acidic phosphorus portion being in a range from about 0.05 to about 4.7% by weight of said mixture.

2. An antioxidant composition comprising a mixture consisting essentially of (1) an arylamine antioxidant por-

7. An antioxidant composition comprising a mixture consisting essentially of (1) an arylamine antioxidant por-

12. An antioxidant composition comprising a mixture consisting essentially of (1) an arylamine antioxidant portion consisting essentially of N-ethylphenothiazine and p,p'-diocetylphenylamine, the weight ratio of said N-ethylphenothiazine to said p,p'-diocetylphenylamine being in a range from about 2:3 to about 3:2, and (2) an acidic phosphorus portion consisting essentially of bis-(2-ethylhexyl)hydrogen phosphite, the concentration of said arylamine antioxidant portion being in a range from about 97.6 to about 99.75% by weight of said mixture and the concentration of said acidic phosphorus portion being in a range from about 0.25 to about 2.4% by weight of said mixture.

13. An antioxidant composition comprising a mixture consisting essentially of (1) an arylamine antioxidant portion consisting essentially of N-dodecylphenothiazine and p,p'-dioctyldiphenylamine, the weight ratio of said N-dodecylphenothiazine to said p,p'-dioctyldiphenylamine being in a range from about 2:3 to about 3:2, and (2) an acidic phosphorus portion consisting essentially of ethyl acid phosphate, the concentration of said arylamine antioxidant portion being in a range from about 97.6 to about 99.75% by weight of said mixture and the concentration of said acidic phosphorus portion being in a range from about 0.25 to about 2.4% by weight of said mixture.

14. A synthetic lubricant consisting essentially of (A) an organic ester base stock and (B) at a concentration in a range from about 0.20 to about 4.05% by weight of said organic ester base stock a mixture consisting essentially of (1) an arylamine antioxidant portion consisting essentially of (a) N-alkylphenothiazine wherein the N-alkyl group has 1-18 carbon atoms and (b) p,p'-dialkyldiphenylamine wherein the p and p'-alkyl groups each have 1-18 carbon atoms, the weight ratio of the N-alkylphenothiazine to the p,p'-dialkyldiphenylamine being in a range from about 1:3 to about 3:1, and (2) an acidic phosphorus portion consisting essentially of ethyl acid phosphate, the concentration of said arylamine antioxidant portion being in a range from about 95.3 to about 99.95% by weight of said mixture and the concentration of said acidic phosphorus portion being in a range from about 0.05 to about 4.7% by weight of said mixture.

15. A synthetic lubricant consisting essentially of (A) an organic ester base stock and (B) at a concentration in a range from about 0.20 to about 4.05% by weight of said organic ester base stock a mixture consisting essentially of (1) an arylamine antioxidant portion consisting essentially of (a) N-alkylphenothiazine wherein the N-alkyl group has 1-18 carbon atoms and (b) p,p'-dialkyldiphenylamine wherein the p and p'-alkyl groups each have 1-18 carbon atoms, the weight ratio of the N-alkylphenothiazine to the p,p'-dialkyldiphenylamine being in a range from about 2:3 to about 3:2, and (2) an acidic phosphorus portion consisting essentially of ethyl acid phosphate, the concentration of said arylamine antioxidant portion being in a range from about 97.6 to about 99.75% by weight of said mixture and the concentration of said acidic phosphorus portion being in a range from about 0.25 to about 2.4% by weight of said mixture.

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