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3,197,408

## SYNTHETIC FUNCTIONAL FLUIDS

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This invention relates to lubricating oil compositions of good viscosity and anti-sludging characteristics, and more particularly, to the improvement of providing lubricating oil compositions having improved anti-corrosive action on metals.

A wide variety of ester type synthetic lubricants are known in the art as being useful as lubricants for aircraft turbine engines having high compression ratios and increased power outputs, such as turbojet and turboprop combustion engines. The use of synthetic esters has made it possible to extend the range of ambient temperatures encountered and allow increased engine operating temperatures.

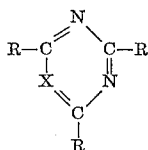
However, the synthetic esters commonly employed as lubricants suffer from the disadvantage of being corrosive towards metal, particularly at high temperatures. It is immediately apparent that much damage can occur to vital parts of an engine by the use of lubricants which have corrosive action towards metal.

Accordingly, it is the object of this invention to provide lubricating oil compositions offering increased corrosion protection towards metals.

It has now been found that the anti-corrosion characteristics of synthetic esters can be markedly improved by the addition to, or the treatment of, said esters with certain nitrogen-containing heterocyclic compounds.

The nitrogen-containing heterocyclic compounds useful for the preparation of improved ester lubricants can be represented by the following formulas:

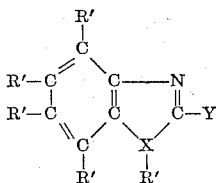
(1)



wherein X represents nitrogen or sulfur and R represents a phenyl radical or the radical  $\text{N}(\text{R}')_2$  wherein  $\text{R}'$  represents hydrogen or an alkyl radical having from 1 to 8 carbon atoms with the proviso that at least one R must be  $\text{N}(\text{R}')_2$ .

Specific compounds encompassed by this formula include melamine,  $\text{N,N',N''}$ -triphenylmelamine and benzoguanamine.

(2)

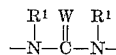


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wherein X represents nitrogen or sulfur and Y represents hydrogen or  $\text{N}(\text{R}')_2$  wherein  $\text{R}'$  represents hydrogen or an alkyl group having from 1 to 8 carbon atoms.

Specific compounds encompassed by this formula include benzimidazole and 2-aminobenzothiazole.

(3) Compounds containing the linkage



as part of the heterocyclic ring structure. In the above formulas, W represents oxygen or sulfur, and  $\text{R}^1$  represents hydrogen or alkyl groups having from 1 to 8 carbon atoms. The compounds represented by (3) can be varied since the only important feature is the presence of the above-mentioned linkages. Examples of compounds represented by (3) include cyanuric acid, alloxantin, ethylene urea, ethylene thiourea, allantoin, acetylene diurene, barbituric acid and barbital.

The improved lubricants of this invention are conveniently prepared by incorporating from 0.01 to 1.0 percent and preferably 0.05 to 0.25 percent by weight of the nitrogen containing heterocyclic compounds with a synthetic base fluid or mixtures of synthetic base fluids and heating for 5 to 30 minutes at a temperature within the range of 100° and lower to 200° C. and higher. Since most of the nitrogen-containing compounds are not entirely soluble in the base fluid to which they are added, it is desirable to filter out the undissolved material after the fluid has been treated.

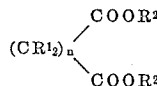
The reasons why the treatment of base fluids with the described nitrogen-containing compounds is effected is not completely understood. However, the fact remains that lubricants are obtained which have superior anti-corrosive properties.

The term base fluid, as used in the specification and the claims, refers to synthetic esters including diesters polyesters, and polyglycol derivatives which are used as bases for lubricants.

The synthetic base fluids to which the nitrogen-containing heterocyclic compounds are added are well known in the art. It is to be understood that the novel lubricants of this invention contain a base fluid or mixtures of base fluids which are conventional. The instant invention does not reside in the particular base fluids, but rather in the treatment of conventional base fluids to obtain lubricants having superior anti-corrosive action on metals, particularly copper and lead.

The base fluids which can be treated according to the invention include:

(A) Diesters of aliphatic dicarboxylic acids which correspond to the general formula:



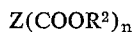
wherein  $n$  is an integer from 2 to 18, preferably from 2 to 12, each  $\text{R}^2$  represents alkyl or cycloalkyl radicals having from about 5 to 24 carbon atoms, and preferably from about 5 to 18 carbon atoms, and  $\text{R}'$  represents hydrogen or alkyl groups having from 1 to 4 carbon atoms. The dicarboxylic acids may be substituted, such as, for example, 3-methyl glutaric acid, to obtain lower viscosities at low temperatures so long as this substitution is consistent with the need for obtaining a low freezing point. Specific examples of organic dicarboxylic acids from which

the esters may be derived are suberic, adipic, brassilic, Japanic, sebacic, glutaric, azelaic, and pimelic acids, as well as mixtures of these acids. The preferred acids are azelaic, adipic, and sebacic acids.

The alcohols used to form the diester of the acid may be branched chain or straight chain, saturated or unsaturated, aliphatic or cycloaliphatic alcohols. Typical alcohols which may be employed include 2-ethylhexyl alcohol, isoocetyl alcohol, isodecyl alcohol, 2-ethylbutyl alcohol, cetyl alcohol, n-octyl alcohol, amyl alcohol, oleyl alcohol, 2-butyloctyl alcohol, methyl and dimethyl cyclohexanol, and the "Oxo" alcohols, such as the mixed branched chain nonanols, prepared from the reaction of carbon monoxide and hydrogen upon olefins which normally have a branched chain structure. Mixtures of alcohols can also be used such as a mixture of 2-ethylhexyl and isodecyl alcohol.

Representative synthetic diester lubricants which can be employed in conjunction with this invention include di-(2-ethylhexyl)sebacate, di-(2-ethylhexyl)azelate, di-[mixed-(2-ethylhexyl, isodecyl)]azelate, di-(isoocetyl)azelate, di-(1-methylcyclohexylmethyl)sebacate, di-(2-ethylhexyl decyl)-azelate, di-(2-ethylhexyl-2-propylheptyl)azelate, di-(2,2,4-trimethylpentyl)sebacate, di-(2-methylpentyl decyl)azelate, di-(1-ethylpropyl)adipate, di-(3-methylbutyl)adipate, di-(1,3-dimethylbutyl)adipate, di-(2-ethylbutyl)adipate, di-(2-ethylhexyl)adipate, di-(isoocetyl)adipate, di-(undecyl)adipate, di-(tetradecyl)adipate, di-(heptadecyl)adipate, di-(2,2,4-trimethylphenyl)adipate, di-(1-methylcyclohexylmethyl)adipate, di-(1-ethylpropyl)azelate, di-(3-methylbutyl)azelate, di-(2-ethylbutyl)azelate, di-(1-ethylpropyl)sebacate, di-(3-methylbutyl)sebacate, di-(1,3-dimethylbutyl)sebacate, di-(2-ethylbutyl)sebacate, di-(2-ethylhexyl)sebacate, di-(2-(2'-ethylbutoxy)ethyl)sebacate, di-(undecyl)sebacate, di-(tetradecyl)sebacate, di-(heptadecyl)sebacate, di-(2-ethylhexyl)glutarate, di-(undecyl)glutarate, di-(tetradecyl)glutarate, and the like.

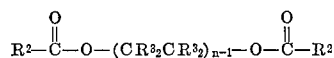
(B) Esters of aromatic acids which correspond to the general formula:



wherein Z represents a phenyl radical or a naphthyl radical,  $n$  represents an integer from 2-4 and  $\text{R}^2$  has the same meaning as previously described.

Examples of acids from which the esters can be prepared include phthalic, terephthalic, pyromellitic, naphthalene-1,4-dicarboxylic acid, etc. The alcohols which are reacted with the aromatic acids are the same as those mentioned under (A).

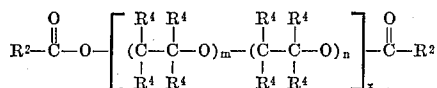
(C) Complex glycol centered esters having the general formula:



wherein  $n$  represents a number from 3-51,  $\text{R}^2$  represents alkyl or cycloalkyl radicals having from 4 to 24 carbon atoms and  $\text{R}^3$  represents hydrogen, methyl or ethyl.

Examples of the above esters include 3-methyl-1,5-pentanediol diisodecanoate and hexamethylene 1,6-glycol diisooctanoate.

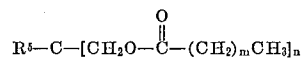
(D) Complex glycol centered esters containing recurring ether linkages represented by the formula:



wherein  $\text{R}^2$  represents alkyl or cycloalkyl radicals having from 4 to 24 carbon atoms,  $\text{R}^4$  represents hydrogen, methyl, or ethyl and wherein  $n$ ,  $m$  and  $X$  represent an integer from 1-25.

Examples of the above esters include dipropylene glycol dipelargonate, polyethylene glycol 200 di-valerate and polypropylene glycol 425 di-2-ethyl hexanoate.

(E) Polyol monobasic acid esters corresponding to the formula:



wherein  $n$  is an integer from 3 to 4 and  $\text{R}^5$  represents an alkyl group having from 0-8 carbon atoms, with the proviso that when  $\text{R}^5$  is 0,  $n$  is 4, and  $m$  is an integer from 0 to 18.

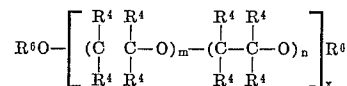
Examples of alcohols which are reacted with aliphatic monocarboxylic acids include trimethylol ethane, trimethylol propane and pentaerythryol.

It is to be understood that the above classes of base fluids are representative of art recognized fluids and are merely illustrative of some of the base fluids useful in this invention. The complex esters have been described in the art as well as in U.S. Patents 2,575,195; 2,575,196; and 2,703,811.

(F) *Alkyl terminated polyesters*.—These are complex polyesters prepared from polyhydric alcohols and polybasic acids wherein reactive carboxyl or hydroxyl groups are terminated by reaction with either monofunctional alcohols or acids. These esters are known in the art and described in U.S. Patent 2,705,724. The disclosure of said patent is incorporated by reference into this application.

(G) *Non-terminated or hydroxyl terminated polyesters*.—This class of compounds refers to those polyesters having free hydroxyl groups in the polymer chain which are blocked or terminated by reaction with monofunctional or polyfunctional compounds. These compounds are known in the art and can be prepared by reacting a dibasic acid with a glycol or alkane diol as disclosed in U.S. Patent 2,929,786 or by reacting a dibasic acid with mixtures of polypropylene glycol and a 1,3-alkanediol as disclosed in copending application Ser. No. 718,971, filed March 4, 1958, and now abandoned.

(H) *Polyalkylene glycol derivatives*.—These compounds can be represented by the formula:



wherein  $\text{R}^6$  represents hydrogen or an alkyl radical having from 1-12 carbon atoms,  $\text{R}^4$  represents hydrogen or an alkyl radical having from 1-2 carbon atoms and each of  $n$ ,  $m$  and  $X$  represent a positive integer from 1-25.

The integers  $m$  and  $n$  can be varied so as to provide homo- and heteropolymers, i.e., polyoxyethylene glycols, polyoxypropylene glycols, mixed poly(oxyethylene-oxypropylene) glycols and also the mono- and diethers of the above.

This class of compounds is well-known in the art and the individual members of this class can be made in a variety of ways. Illustrative of the above class of compounds, as well as methods for the preparation of individual members are U.S. Patents 2,293,868; 2,425,755; 2,425,845; 2,448,664; 2,520,611 and 2,520,612.

The preferred compounds in this class are the mono-butyl ethers.

It is to be understood that this invention relates to the treatment of base fluids in a novel manner and not to the particular base fluids employed. Thus, the above class of base fluids ((A) to (H)) are representative of base fluids which can be treated according to the novel process of this invention. It is also within the scope of this invention to treat mixtures of base fluids which have been designated by (A) to (H).

It is to be understood that the novel lubricants of this invention can contain conventional additives, e.g., viscosity index improvers, detergents and antioxidants, as is customary in this art. The preferred antioxidants are amine compounds such as phenothiazine, N-phenyl-beta-naphthylamine, N-phenyl-alpha-naphthylamine, and phenolic compounds such as di-tert-butyl para-cresol and butylated hydroxyanisole.

The following table depicts the critical specifications of a gas turbine lubricant and is based upon U.S. Specification Mil-L-7808C. Somewhat similar specifications are required for turboprop lubricants as described by EMS 35E of the Allison Division of General Motors Corporation and Specification D. Eng. R.D. 2487 (Second Issue) of the British Ministry of Supply.

TABLE I.—CRITICAL GAS TURBINE AIRCRAFT LUBRICANT SPECIFICATIONS

Corrosion and oxidation	Standard 347 °F. test	352 °F. test
Weight Change, mg./sq. cm.:		
Copper	±0.4	±0.4
Magnesium	±0.2	
Aluminum	±0.2	
Steel	±0.2	±0.2
Silver	±0.2	
Lead		±1.0
Viscosity change, 100° F., percent	-5 to +15	-5 to +15
Neut. No. increase, mg. KOH/g.	2.0	2.0
SOD lead corrosion, 1 hr. at 325° F., mg./sq. in.		6.0 (Max.)
Corrosion, 50 hr. at 450° F., mg./sq. in.:		
Copper		3.0 (Max.)
Silver		3.0 (Max.)
Panel coking—8 hours at 600° F.		80.0 (Max.)

### Test methods

The 352° F. corrosion and oxidation test was employed as the primary tool to evaluate urea-treated fluids. The 352° F. test, designed to simulate the standard military corrosion and oxidation test (791.5308.4) was simplified by eliminating aluminum, magnesium, and silver metals, and adding a lead specimen. Steel and copper coupons are used in both tests. The 352° F. test consists of maintaining the test fluid at test temperature in the presence of the steel, copper, and lead specimens for 72 hours while purging with air at the rate of 5 liters per hour. At the completion of the test, the fluid is observed for the separation of insolubles and for viscosity change. The weight change of the metal specimens is also determined.

The SOD (Standard Oil Development Company) lead corrosion test was also used. This is the standard test procedure employed by the military for evaluating the tendency of gas turbine lubricants to corrode lead. The Allison Division (General Motors Corporation) aircraft gas turbine lubricant specifications include the SOD lead corrosion test. This test consists in rotating copper and lead (weighed) specimens for one hour in the test fluid which is maintained at 325° F. During the test, air is passed through the fluid at a rate of 57 liters per hour. The weight change of the lead specimen, in milligrams per square inch, is determined. At the present time, all lubricant specifications containing this test allow a maximum lead corrosion value of 6.0 milligrams per square inch. Values under 1.0 milligram per square inch are highly desirable.

The following tables illustrate the improved properties of the novel lubricants of this invention.

TABLE II.—MELAMINE TREATMENT OF ALIPHATIC DIBASIC ACID ESTERS

Antioxidant=0.5% N.F. purified phenothiazine.

352° F. corrosion and oxidation test data—Fe, Cu, and Pb metals present

Diester	Melamine wt. percent	Treating condition		Percent vis. change 100° F.	Insolubles	Metal condition		Metal weight change, mg./cm. <sup>2</sup>		
		Temp., ° C.	Time, min.			Copper	Lead	Steel	Copper	Lead
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,2</sup>	None			+2.2	Moderate	Dull bronze	Gray-black	+0.05	Nil	-0.37
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,2</sup>	None			+4.5	do.	Dull brown-Cu.	do.	+0.04	-0.08	-1.6
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,3</sup>	0.05	110-120	15-20	+4.4	do.	Dull orange-Cu.	Dark gray-black.	+0.03	-0.04	-2.66
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,3</sup>	None			+11.9	do.	Dull orange.	G-BK <sup>6</sup> pitted.	Nil	-0.52	-8.0
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,3</sup>	0.05	110-120	15-20	+0.04	do.	Dull	Dull gray	+0.04	-0.06	-0.69
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,4</sup>	None			+2.7	do.	do.	Almost black.	+0.03	-0.12	-3.1
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,4</sup>	0.05	110-120	15-20	+2.3	do.	Dull brown.	G-BK	+0.05	-0.03	-0.68
C <sub>8</sub> -azelate <sup>5</sup>	None			+19.9	Large	Pale	BK-Rough crust.	+0.02	-15.9	-25.9
C <sub>8</sub> -azelate <sup>5</sup>	0.05	110-120	15-20	+40.2	Moderate	Dull brown.	do.	+0.02	-1.8	-36.4
C <sub>8</sub> -azelate <sup>5</sup>	0.50	110-120	15-20	+28.1	do.	do.	Bright	Nil	-7.1	-45.4
Di-2-ethylhexyl adipate	None			+2.7	do.	Dull pink-Cu.	Shiny	+0.04	Nil	-2.3
Di-2-ethylhexyl adipate	0.05	110-120	15-20	+1.5	do.	Yellow-copper.	G-BK.	-0.06	+0.06	-1.6

<sup>1</sup> Di-(2-ethylhexyl, isodecyl)azelate.

<sup>2</sup> Prepared by acid catalysis and hydrogenation refining.

<sup>3</sup> Tetra-butylorthotitanate-catalyzed residue preparation.

<sup>4</sup> Tetra-butylorthotitanate-catalyzed distilled preparation.

<sup>5</sup> Di-2-ethylhexylazelate. Prepared by acid catalysis.

<sup>6</sup> G-BK=Gray Black.

TABLE III.—MELAMINE TREATMENT OF ALIPHATIC DIBASIC ACID ESTERS

Antioxidant=0.5% N.F. purified phenothiazine.  
352° F. corrosion and oxidation test data—Fe, Cu, and Pb metals present

Diester	Melamine wt. percent	Treating condition		Percent vis. change 100° F.	Insolubles	Metal condition		Metal weight change, mg./cm. <sup>2</sup>		
		Temp., ° C.	Time, min.			Copper	Lead	Steel	Copper	Lead
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,2</sup>	None			+2.2	Moderate	Dull bronze.	Gray-black	+0.05	Nil	-0.37
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,2</sup>	None			+4.5	do	Dull brown-Cu.	do	+0.04	-0.08	-1.6
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,2</sup>	0.05	110-120	15-20	+4.4	do	Dull orange-Cu.	Dark gray-black.	-0.03	-0.04	-2.66
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,3</sup>	None			+11.9	do	Dull orange.	G-BK <sup>6</sup> pitted.	Nil	-0.52	-8.0
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,3</sup>	0.05	110-120	15-20	+0.04	do	Dull	Dull gray	+0.04	-0.06	-0.69
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,4</sup>	None			+2.7	do	do	Almost black.	+0.03	-0.12	-3.1
C <sub>8</sub> -C <sub>10</sub> azelate <sup>1,4</sup>	0.05	110-120	15-20	+2.3	do	Dull brown.	G-BK	+0.05	-0.03	-0.68
C <sub>8</sub> -azelate <sup>5</sup>	None			+19.9	Large	Pale	BK-Rough crust.	+0.02	-15.9	-25.9
C <sub>8</sub> -azelate <sup>5</sup>	0.05	110-120	15-20	+40.2	Moderate	Dull brown.	do	+0.02	-1.8	-36.4
C <sub>8</sub> -azelate <sup>5</sup>	0.50	110-120	15-20	+28.1	do	do	Bright	Nil	-7.1	-45.4
Di-2-ethylhexyl adipate	None			+2.7	do	Dull pink-Cu.	Shiny	+0.04	Nil	-2.3
Di-2-ethylhexyl adipate	0.05	110-120	15-20	+1.5	do	Yellow-copper.	G-BK.	-0.06	+0.06	-1.6

<sup>1</sup> Di-(2-ethylhexyl, isodecyl)azelate.

<sup>2</sup> Prepared by acid catalysis and hydrogenation refining.

<sup>3</sup> Tetra-butylorthotitanate-catalyzed residue preparation.

<sup>4</sup> Tetra-butylorthotitanate-catalyzed distilled preparation.

<sup>5</sup> Di-2-ethylhexylazelate. Prepared by acid catalysis.

<sup>6</sup> G-BK=Gray Black.

TABLE IV.—NITROGEN-CONTAINING HETEROCYCLICS AS CORROSION INHIBITORS FOR DIESTERS

352° F. corrosion and oxidation test  
Base fluid—di-2-ethylhexyl azelate  
Antioxidant—0.5% (wt.) N.F. purified phenothiazine  
Treating conditions—15-20 minutes at 115°-120° C.

Treating compound <sup>1</sup>	Weight Percent	Percent vis. change 100° F.	Insolubles	Metal condition		Metal weight change mg/cm. <sup>2</sup>		
				Copper	Lead	Steel	Copper	Lead
None		+19.7	Large	Pale	Black rough crust. <sup>4</sup>	+0.02	-15.9	-25.9
Melamine	0.05	+40.2	do	Dull brown	do	+0.02	-1.8	-36.9
Benzimidazole <sup>2</sup>	0.10	+18.9	do	Pale tar-nished.	Bright	Nil	-0.14	-23.5
2-aminobenzothiazole <sup>2</sup>	0.01	+19.1	do	Brown	do	-0.02	-14.9	-13.4
2-aminobenzothiazole	0.10	+7.2	do	do	do	+0.02	-3.4	-14.8
Cyanuric acid <sup>3</sup>	0.05	+32.3	do	Pink-copper.	Bright black spots.	+0.05	-0.53	-4.4
Cyanuric acid	0.10	+40.3	do	Brown	Bright	+0.03	-0.70	-12.0
Barbituric acid	0.10	+23.0	do	Dull pink-copper.	do	+0.04	-0.18	-41.3
Brabital	0.10	+23.1	Moderate-large.	Light copper.	do	Nil	-22.8	-12.3
Allantoin	0.10	+26.9	do	Pink-copper.	do	+0.02	-17.8	-8.1
Alloxantin	0.10	+45.8	do	do	do	+0.03	-9.5	-19.9
N,N',N"-Triphenylmelamine	0.10	+23.0	Moderate	Light copper.	do	Nil	-14.3	-5.2

<sup>1</sup> All additives insoluble in the diester unless otherwise noted.

<sup>2</sup> Soluble in diester.

<sup>3</sup> Very slightly soluble.

TABLE V.—NITROGEN-CONTAINING HETERO-CYCLICS AS CORROSION INHIBITORS FOR DIESTERS

352° F. corrosion and oxidation test  
Base fluid—di-(2-ethylhexyl, isodecyl)azolate  
Antioxidant—0.5% (Wt.) N.F. purified phenothiazine  
Treating conditions—15-20 minutes at 115-120° C.

Treating compound <sup>1</sup>	Weight Percent	Percent vis. change 100° F.	Insolubles	Metal condition		Metal weight change mg./cm. <sup>2</sup>		
				Copper	Lead	Steel	Copper	Lead
1. None.....		+4.5	Moderate.....	Dull Brown-Copper.	G-BK <sup>2</sup> .....	+0.04	-0.08	-1.6
2. Melamine.....	0.05	+4.4	.....do.....	Dull Orange-Copper.	Dark G-BK.	+0.03	-0.04	-2.66
3. Cyanuric acid.....	0.05	+3.8	Small to moderate.	Dull Brown-Copper.	Dull gray.....	Nil	-0.09	-0.11
4. Acetylene diurene.....	0.05	+6.8	.....do.....	Brown-Copper.	G-BK.....	+0.02	-0.08	-1.06
5. Benzoguanamine <sup>3</sup> .....	0.05	+2.5	.....do.....	Red-Brown.	Brown-Black.	Nil	Nil	-2.53
6. Benzimidazole.....	0.05	+3.7	Small.....	Dull.....	Dull gray.....	Nil	-0.01	-0.10
7. Benzimidazole.....	0.05	+2.8	.....do.....	Gold-Copper.	Dark gray.....	Nil	-0.05	-0.19
8. Benzimidazole.....	0.05	+2.8	Small to moderate.	.....do.....	.....do.....	Nil	-0.04	-0.21
Cyanuric acid.....	0.05							
Hydantoin.....	0.50							

<sup>1</sup> Additives essentially insoluble, unless otherwise noted.

<sup>2</sup> Gray-Black.

<sup>3</sup> Soluble.

TABLE VI.—TREATMENT OF MISCELLANEOUS COMPLEX ESTERS

352° F. corrosion and oxidation tests—steel, copper and lead present  
Antioxidant—0.5% N.F. purified phenothiazine

Complex ester	Treating compound wt. percent	Treating condition		Percent vis. change 100° F.	Insolubles	Metal condition		Metal weight change mg./cm. <sup>2</sup>		
		Temp ° C.	Time, min.			Copper	Lead	Steel	Copper	Lead
1. Polyester <sup>1</sup> .....	None.....			+14.9	Small.....	Dull pale.	G-BK <sup>2</sup> .....	Nil	-3.2	-6.1
2. Polyester <sup>1</sup> .....	Melamine 0.05.....	110-120	20	+1.3	Very small.....	Gold-Copper.	G-BK.....	Nil	-0.04	-3.1
3. Polyester <sup>3</sup> .....	None.....			+5.0	Small to moderate.	Dull.....	Dull gray.....	Nil	-0.07	-0.14
4. Polyester <sup>3</sup> .....	Benzimidazole, 0.05, Cyanuric Acid, 0.05.	110-120	20	+4.7	.....do.....	Gold-Copper.	Dull-light gray.	+0.02	+0.02	-0.08.
5. Polyester <sup>4</sup> .....	None.....			+2.0	None.....	Pale Pink.	G-BK.....	Nil	-0.24	-1.24
6. Polyester <sup>4</sup> .....	Benzimidazole, 0.05, Cyanuric Acid, 0.05.	110-120	20	-11.7	Small.....	Orange Copper.	Light Brown-Cu.	Nil	Nil	-0.28
7. Polyester <sup>4</sup> .....	Ethylene Urea, 0.05.	110-120	20	-1.8	V. Small.....	Dull.....	G-BK.....	Nil	-0.23	-0.92
8. Polyester <sup>4</sup> .....	Ethylene-Thiourea, 0.05.	110-120	20	+4.6	Moderate.....	Dull, Pale Etched.	.....do.....	Nil	-1.09	-0.79
9. Polyester <sup>4</sup> .....	None.....			-1.4	None.....	Dull, Pale.	Bright Silver-blue.	Nil	-0.24	-0.04
10. Polyester <sup>4</sup> .....	Benzoguanamine 0.05.	110-120	20	-0.54	.....do.....	Dull.....	.....do.....	Nil	-0.18	-0.04

<sup>1</sup> Prepared by reacting adipic acid, 3-methylpentanediol-1,5, and iso-decylalcohol (OXO) in a 1.0:0.66:0.83 mol ratio.

<sup>2</sup> Gray-Black.

<sup>3</sup> 1,2,6-Hexanetriol 2-ethylhexylazolate. (triester).

<sup>4</sup> Tested in blend containing 80% C<sub>8</sub>-C<sub>10</sub>-Azolate, 19.5% Polypropylene glycol 425 azelate, and 0.5% Phenothiazine.

TABLE VII.—CRITICAL SPECIFICATION TEST DATA ON ESTER-TYPE FLUIDS TREATED WITH MELAMINE

SAMPLES CONTAINED 0.5% PURIFIED PHENOTHIAZINE

Property	C <sub>8</sub> C <sub>10</sub> Azelate	* TBP-F-2 lubricant
Acid number, mg. KOH/g.....	0.06	0.07
Viscosity, cks.:		
210° F.....	3.29	7.71
100° F.....	12.60	34.69
-40° F.....		3563
-65° F.....	9782	
Flash point, ° F.....	440	
Fire point, ° F.....	475	
SOD lead corrosion, mg./sq. in.....	3.1	4.7
Corrosion after 50 hr. at 450° F., mg./sq. in.:		
Copper.....	0.2	0.3
Lead.....	++++	0.1
Corrosion-oxidation at 347° F.—wt. changes, mg./sq. cm.:		
Copper.....	nil.	0.0
Magnesium.....	nil	nil
Aluminum.....	nil	0.0
Steel.....	nil	0.0
Silver.....	nil	nil
100° F. viscosity change, percent.....	+2	-3
Neut. No. increase, mg. KOH/g.....	1.1	0.8
Panel coking, 8 hrs. at 600° F., mg.....	12.8	15.9

\* See the following table:

	Weight percent
C <sub>8</sub> -C <sub>10</sub> Azelate.....	79.6
Melamine treated polypropylene glycol 425 Azelate.....	19.9
N. F. purified phenothiazine.....	0.5

The following examples will illustrate the actual preparation of the novel lubricants.

#### EXAMPLE I

Di-(2-ethylhexyl, isodecyl) azelate was prepared as a residue product by reacting commercial grade azelaic acid with isodecyl alcohol (from the "Oxo" process) and an excess of 2-ethylhexanol in the presence of a catalytic amount of tetrabutyl orthotitanate, removing the water of reaction by suitable means. After a sufficiently low acid number was achieved, the reaction was stopped, the excess 2-ethylhexanol was stripped from the reaction mixture and the product filtered through a diatomaceous-silica filter bed resulting in diester A. The diester had viscosities of 3.37, 13.10, and 10,559 centistokes at 210°, 100° and -65° F., respectively. A portion of this diester was treated with 0.05 percent melamine by mixing thoroughly at 110° C. for a period of 15 minutes and filtering (Diester B). Diesters A and B were submitted to a corrosion and oxidation test at 352° F. in the presence of metallic steel, copper, and lead. The test consisted of passing air through 100 grams of the test fluid contained in a flask equipped with a reflux condenser and thermometer. After the test, the weight change of the metals and the viscosity change of the fluid were determined. Test data are shown in the following table:

	Ester A+0.5% (wt.) purified phenothiazine	Ester B+0.5% (wt.) purified phenothiazine
Viscosity change, 100° F., percent.....	+11.9	+4.1
Insolubles.....	Moderate amount	Moderate amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	Nil	+0.04
Copper.....	-0.52	-0.06
Lead.....	-8.0	-0.69

#### EXAMPLE II

A portion of the residue diester from Example No. 1 was distilled under vacuum to produce a product having viscosities of 3.29, 12.70, and 9686 centistokes at 210°, 100°, and -65° F., respectively. This diester was called Ad. A portion of the distilled product was treated with 0.05 percent melamine for 15 minutes at 110° C. followed by filtration (diester Bd). Corrosion and oxidation test

data for the distilled diesters are shown in the following table:

	Ester Ad+0.5% (wt.) purified phenothiazine	Ester Bd+0.5% (wt.) purified phenothiazine
Viscosity change, 100° F., percent.....	+2.7	+2.3
Insolubles.....	Moderate amount	Moderate amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	+0.03	+0.05
Copper.....	-0.124	-0.03
Lead.....	-3.1	-0.68

#### EXAMPLE III

A sample of distilled di - [mixed - (2 - ethylhexyl, isodecyl)] azelate was prepared by a conventional esterification procedure, using sulfuric acid as a catalyst. The product (Ester C) had viscosities of 3.26 and 12.3 centistokes at 210° and 100° F., respectively. A portion of this diester was treated by mixing thoroughly with 0.05 percent melamine for 15 minutes at 115° C. followed by filtration (Ester D). Corrosion and oxidation test data are shown in the following table:

	Ester C+0.5% phenyl beta naphthylamine +0.25% purified phenothiazine	Ester D+0.5% phenyl beta naphthylamine +0.25% purified phenothiazine
Viscosity change, 100° F., percent.....	+28.5	+11.2
Insolubles.....	Moderately large amount	Large amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	Nil	Nil
Copper.....	-9.76	-0.05

#### EXAMPLE IV

A sample of di-[mixed-(2-ethylhexyl, isodecyl)] azelate was synthesized by tetrabutyl orthotitanate catalysis in the presence of 0.05 percent melamine. Except for the addition of melamine, this diester was treated the same as for Ester A. The diester (Ester E) which had viscosities of 3.37, 12.56, and 10386 at 210°, 100°, and -65° F., respectively, had corrosion and oxidation characteristics as shown in the following table:

	Ester E+0.5% (wt.) phenothiazine
Viscosity change at 100° F., percent.....	2.9
Insolubles.....	Moderate amount
Metal weight change, mg./cm. <sup>2</sup> :	
Steel.....	Nil
Copper.....	Nil
Lead.....	-0.77

#### EXAMPLE V

A sample of commercial di-2-ethylhexyl adipate (Ester F) was subjected to the corrosion and oxidation test together with a sample of the same ester which was treated with 0.05 percent melamine for 10 minutes at 105-110° C. (Ester G). Treatment was melamine improved the corrosion and oxidation stability of the diester as shown by the data in the following table:

	99.5% (wt.) Ester F, 0.5% (wt.) phenothiazine	99.5% (wt.) Ester G, 0.5% (wt.) phenothiazine
Viscosity change at 100° F., percent.....	+2.7	+1.5
Insolubles.....	Small amount	Small amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	+0.04	-0.06
Copper.....	Nil	+0.06
Lead.....	-2.3	-1.6

#### EXAMPLE VI

A hydroxyl-terminated polyester was prepared by reacting a polyoxy-1,2-propylene glycol having a molecular

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weight of approximately 425 and azelaic acid in a 1:1.15 molar ratio. The product (code: Polyester P) had viscosities of 181 and 1838 centistokes at 210° F. and 100° F., respectively, and an acid number of 0.06. A portion of the polyester was treated by stirring at 120° C. for 15 minutes in the presence of 0.05 percent melamine followed by filtration through a bed of powdered diatomaceous silica. (This polyester is referred to as Polyester Q.) Each of these polyesters was blended with a sufficient quantity of di-[mixed-(2-ethylhexyl, isodecyl)] azelate to meet the 7.5 centistokes at 210° F. minimum viscosity requirement for commercial turboprop aircraft lubricants. This polyester-diester blend was subjected to the corrosion-oxidation test referred to above with the results which are shown in the following table:

	81.5% (wt.) diester, 18.0% (wt.) P, 0.5% (wt.) purified phenothiazine	81.5% (wt.) diester, 18.0% (wt.) Q, 0.5% (wt.) purified phenothiazine
Viscosity change at 100° F., percent.....	-1.3	-1.4
Insolubles.....	None	Small amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	Nil	Nil
Copper.....	-0.18	-0.06
Lead.....	-3.1	-0.82

## EXAMPLE VII

A complex ester was prepared by reacting adipic acid, 3-methyl-1,5-pentanediol, and isodecyl alcohol (Oxo) in a molar ratio of 1.0 to 0.66 to 0.83 in the presence of tetrabutyl ortho-titanate as the catalyst. This complex ester (Ester R) had viscosities of 15.17 and 97.18 centistokes at 210° F. and 100° F., respectively, and an acid number of 0.48. A sample of ester R was treated with 0.05 percent melamine by mixing thoroughly for 15 minutes at 110° C. (Ester S). The data in the following table illustrate the dramatic improvement obtained by melamine treatment.

	99.5% (wt.) Ester R, 0.5% (wt.) phenothiazine	99.5% (wt.) Ester S, 0.5% (wt.) phenothiazine
Viscosity change at 100° F., percent.....	+14.9	+1.3
Insolubles.....	Small amount	Small amount
Metal weight change, mg./cm. <sup>2</sup> :		
Steel.....	Nil	Nil
Copper.....	-3.16	-0.04
Lead.....	-6.1	-3.1

## EXAMPLE VIII

A sample of polyoxypropylene glycol monobutyl ether having a Saybolt Universal seconds viscosity of approximately 625 ("Ucon" Lubricant LB-625) was inhibited with 0.5 percent of purified phenothiazine and exposed to the 352° F. corrosion-oxidation test and the SOD (Standard Oil Development) lead corrosion test. The results of these tests are compared with similar data obtained with the same fluid to which 0.05 percent each of cyanuric acid and benzimidazole were added. The improvement due to the nitrogen compounds, cyanuric acid and benzimidazole is obvious.

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POLYOXYPROPYLENE GLYCOL "UCON"  
LUBRICANT LB-625

	Weight percent composition	
	99.5% LB-625 0.5% phenothiazine	99.4% LB-625 0.5% phenothiazine 0.05% cyanuric Acid 0.05% benzimidazole
352° F. corrosion-oxidation test—metal weight change, mg./cm. <sup>2</sup> :		
Iron.....	+0.08	+0.01
Copper.....	-0.20	-0.07
Lead.....	-0.53	-0.04
SOD lead corrosion, 2 hrs. at 325° F. mg./in. <sup>2</sup> .....	-3.1	-0.19

## EXAMPLE IX

A fluid composed of 33 percent by weight of a polyoxypropylene glycol monobutyl ether having a Saybolt Universal viscosity of approximately 1145 seconds at 100° F. ("Ucon" Lubricant LB-1145) and 67 percent by weight of di-2-ethylhexyl azelate was inhibited with 0.5 percent by weight of purified phenothiazine and tested by the 352° F. corrosion and oxidation test and the SOD lead corrosion test. Reduction in corrosivity of this blend upon the addition of small concentrations of cyanuric acid and benzimidazole is illustrated in the following table:

"UCON" LUBRICANT LB-1145-DI-2-ETHYL-  
HEXYL AZELATE BLEND

	Weight Percent Composition	
	*99.5% blend 0.5% phenothiazine	*99.4% blend 0.5% phenothiazine 0.05% cyanuric acid 0.05% benzimidazole
352° F. corrosion-oxidation test—metal weight change, mg./cm. <sup>2</sup> :		
Iron.....	Nil	Nil
Copper.....	-0.55	-0.07
Lead.....	-0.04	-0.07
SOD Lead Corrosion, m g./in. <sup>2</sup> .....	-0.73	-0.13

\* 33% (Wt.) "Ucon" LB-1145.  
67% (Wt.) Di-2-Ethylhexyl Azelate.

## EXAMPLE X

A sample of commercial di(isodecyl) adipate prepared from adipic acid and isodecyl alcohol obtained by the "Oxo" process was inhibited with 0.5 percent of purified phenothiazine. A second sample was prepared which contained 0.05 percent cyanuric acid, and a third sample contained 0.05 percent each of cyanuric acid and benzimidazole. The improvement obtained by the addition of the nitrogen-containing heterocyclic compounds is shown by the data in the following table:

## DI-ISODECYL ADIPATE

	Weight percent composition		
	99.5% DIOA <sup>1</sup> 0.5% PHTZ <sup>2</sup>	99.45% DIOA <sup>1</sup> 0.5% PHTZ <sup>2</sup> 0.05% Cyanuric Acid	99.4% DIOA <sup>1</sup> 0.5% PHTZ <sup>2</sup> 0.05% Cyanuric Acid, 0.05% Benzimidazole
352° F. corrosion-oxidation test—Metal weight change, mg./cm. <sup>2</sup> :			
Iron.....	+0.02	+0.02	+0.03
Copper.....	-7.29	-0.21	+0.05
Lead.....	-11.3	-1.96	-3.3
SOD lead corrosion, mg./in. <sup>2</sup> .....	-47.3	-1.86	-2.3

<sup>1</sup> Di-isodecyl Adipate.  
<sup>2</sup> Phenothiazine.

EXAMPLE XI

A lubricant formulation containing 30 percent by weight of di-isodecyl adipate, 69 percent by weight of di-isooctyl adipate, and 1 percent by weight of a polyoxypropylene glycol monobutyl ether having a S.U.S. viscosity at 100° F. of approximately 1715 ("Ucon" Lubricant LB-1715) was tested for corrosiveness towards metals before and after the addition of small concentrations of benzimidazole and cyanuric acid. Phenothiazine was employed as the antioxidant in these compositions. The data in the following table illustrate the improvement in lubricant quality due to the nitrogen-containing heterocyclics.

MIXED ADIPATE DIESTER-"UCON" LUBRICANT LB-1715 BLEND \*

	Weight percent composition	
	99.5% blend 0.5% phenothiazine	99.5% blend 0.5% phenothiazine 0.05% cyanuric acid 0.05% benzimidazole
352° F. Corrosion-Oxidation Test—metal weight change, mg./cm. <sup>2</sup> :		
Iron.....	+0.03	+0.01
Copper.....	-0.20	-0.06
Lead.....	-4.58	-0.16
SOD lead corrosion, mg./in. <sup>2</sup> ..	-39.2	-1.2

\*See the following table:

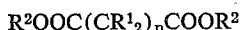
	Percent
DI-isodecyl adipate.....	30
"UCON" LB 1715.....	1
DI-isooctyl adipate.....	69

What is claimed is:

1. A synthetic lubricant composition comprising a synthetic base fluid selected from the group consisting of ester-based fluids and polyalkylene glycol base fluids and a corrosion inhibiting amount for said synthetic base fluid of cyanuric acid as a corrosion inhibitor for said base fluid.

2. The synthetic lubricant composition of claim 1 wherein the corrosion inhibitor is a corrosion inhibiting amount of the combination of cyanuric acid and benzimidazole.

3. The composition of claim 1 wherein the synthetic base fluid corresponds to the formula:



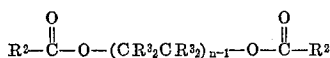
wherein *n* is an integer from 2 to 18, each *R*<sup>2</sup> is individually selected from the group consisting of alkyl and cycloalkyl radicals having from 5 to 24 carbon atoms and *R*<sup>1</sup> is selected from the group consisting of hydrogen and alkyl groups having from 1 to 4 carbon atoms.

4. The composition of claim 1 wherein the base fluid corresponds to the formula:



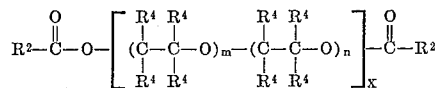
wherein *Z* is a radical selected from the group consisting of a phenyl radical and a naphthyl radicals; *n* represents an integer from 2 to 4; and each *R*<sup>2</sup> is individually selected from the group consisting of alkyl and cycloalkyl radicals having from 5 to 24 carbon atoms.

5. The composition of claim 1 wherein the base fluid corresponds to the formula:



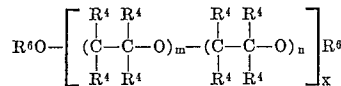
wherein each *R*<sup>2</sup> is selected from the class consisting of alkyl and cycloalkyl radicals having from 4 to 24 carbon atoms, *R*<sup>3</sup> is selected from the class consisting of hydrogen and alkyl groups containing from 1 to 2 carbon atoms, and *n* is an integer from 3 to 51.

6. The composition of claim 1 wherein the base fluid corresponds to the formula:



wherein *R*<sup>2</sup> is selected from the class consisting of alkyl and cycloalkyl radicals having from 4 to 24 carbon atoms, *R*<sup>4</sup> is selected from the class consisting of hydrogen and alkyl groups containing from 1 to 2 carbon atoms, and *n*, *m* and *X* are integers from 1 to 25.

7. The composition of claim 1 wherein the base fluid corresponds to the formula:



wherein *R*<sup>6</sup> is selected from the class consisting of hydrogen and an alkyl radical having from 1 to 12 carbon atoms, *R*<sup>4</sup> is selected from the class consisting of hydrogen and an alkyl radical having from 1 to 2 carbon atoms, and each of *n*, *m* and *X* are positive integers from 1 to 25.

8. The composition of claim 1 wherein the base fluid is a non-terminated polyester.

9. The composition of claim 1 wherein the base fluid is an alkyl-terminated polyester.

10. The composition of claim 1 wherein the base fluid is 2-ethylhexyl, isodecyl azelate.

11. The composition of claim 1 wherein the base fluid is di-2-ethylhexyl adipate.

12. The composition of claim 1 wherein the base fluid is an ester of azelaic acid and a polyoxypropylene glycol having an average molecular weight of 425.

13. The composition of claim 1 wherein the base fluid is a mixture of an ester of azelaic acid and propylene glycol having an average molecular weight of 425 and 2-ethylhexyl, isodecyl azelate.

14. The composition of claim 1 wherein the base fluid is a polypropylene glycol monobutyl ether.

15. The composition of claim 1 wherein the base fluid is a mixture of a polypropylene glycol monobutyl ether and di-2-ethylhexyl azelate.

16. The composition of claim 1 wherein the base fluid is a mixture of di-(isodecyl) adipate, di-(isooctyl) adipate and a polyoxypropylene glycol monobutyl ether having a 100° F. S.U.S. viscosity of 1715.

17. The composition of claim 1 wherein the base fluid is di(isodecyl) adipate.

18. A synthetic lubricant consisting essentially of mixed 2-ethylhexyl, isodecyl esters of azelaic acid and a corrosion inhibiting amount of cyanuric acid.

19. A synthetic lubricant consisting essentially of di(2-ethylhexyl)azelate and a corrosion inhibiting amount of cyanuric acid.

20. A synthetic lubricant consisting essentially of a polyoxypropylene glycol monobutyl ether, and a corrosion inhibiting amount of the combination of cyanuric acid and benzimidazole.

21. A synthetic lubricant consisting essentially of a polyoxypropylene glycol monobutyl ether, di-2-ethylhexyl adipate, and a corrosion inhibiting amount of the combination of cyanuric acid and benzimidazole.

22. A synthetic lubricant consisting essentially of a polyoxypropylene glycol monobutyl ether, di-isodecyl adipate, di-isooctyl adipate, and a corrosion inhibiting amount of the combination of cyanuric acid and benzimidazole.

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