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DI-ESTER FLUIDS WITH IMPROVED WATER TOLERANCE

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This invention generally relates to aliphatic di-ester fluids having improved water tolerance. It is concerned more particularly with mixtures of such di-esters with polyoxyalkylene glycols.

Di-ester type fluids, including substituted adipates, azelates and sebacates, find extensive use as high temperature turbine lubricants for aircraft engines, instruments and in general wherever excellent viscosity-solubility and viscosity-temperature properties are needed. These fluids, however, possess the unwanted tendency of dissolving or absorbing small amounts of water. This solubility decreases at lower temperatures, and condensate absorbed by the fluids at operating temperatures later precipitates as ice after shut down at winter temperatures. Precipitation of the thus formed ice in oil lines or at nozzles can cause clogging.

It has been found that the water tolerance and viscometric stability of the above di-ester fluids can be increased by the addition of polyoxyalkylene glycol derivatives. These derivatives are the addition products formed by the reaction of an alcohol with ethylene oxide, or propylene oxide or a mixture of these oxides in which the ratios of the respective oxides are from about 25 percent–75 percent to 75 percent–25 percent. Such products are viscous liquids of relatively high average molecular weight, and actually are complex mixtures of polyoxyalkylene chains having different lengths. For a further and more detailed description of the additives of the invention, reference is made to U.S. Patents 2,425,755 and 2,425,845, issued August 19, 1947, in the names respectively of F. H. Roberts et al. and W. J. Toussaint et al.

The lubricant fluid of the invention thus comprises a mixture of di-alkyl esters of simple and substituted di-basic acids having from 6 to 10 carbon atoms, and polyoxyalkylene glycols and mono and di-ether derivatives thereof having a viscosity ranging from 59 to 3000 SUS at 100° F.

To illustrate the effectiveness of the additives of the invention in improving the water tolerance of di-esters, cloud point determinations were made on two of these.

TABLE I

Water Content of the Di-Ester (Percent)	Cloud Point on Cooling (° F.)	
	Di-2-ethylhexyl Adipate	Di-2-ethylhexyl Sebacate
0.01 to 0.02	Below −70	Below −65
0.06	−70	−20
0.10	−20	+5
0.20	+40	+75
0.30	+85	+105

The cloud point is the temperature at which a definite turbidity is noted on cooling the fluid. This was determined by observing the sample in a test tube immersed in a cold bath. A thermometer placed in the sample was read when turbidity was first evident.

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Table I indicates that as di-esters absorb water from the atmosphere, their cloud points are raised objectionably. A quantity of di-2-ethylhexyl sebacate as received from a manufacturer contained 0.06 percent water, and di-2-ethylhexyl adipate from another source absorbed 0.09 percent water. Accordingly, both were turbid on standing at about −20° F.

Table II cites examples showing that the water tolerance of di-2-ethylhexyl adipate was increased appreciably by the addition of various polyoxyalkylene glycol derivatives.

"A" is a polyoxypropylene glycol monobutyl ether having a viscosity of 3,000 SUS at 100° F.

"B" is a polyoxypropylene glycol dibutyl ether having a viscosity of 130 SUS at 100° F.

"C" is a butyl ethyl diether of a polyalkylene glycol made from a 50–50 mixture of propylene and ethylene oxide with the final diether having a viscosity of 59 SUS at 100° F.

TABLE II

Examples 1 to 8

Example 1-8	Polyalkylene Glycol Derivative	Cloud Point with Di-2-Ethylhexyl Adipate, ° F.	
		0.11% Water	0.16% Water
1	None	−14	+16
2	2% A	−30	+6
3	5% A	−32	+6
4	10% A	−52	−30
5	5% B	−30	+5
6	10% B	−52	−30
7	20% B	−70	−45
8	10% C		Below −70

Other diesters show similar beneficial effects from addition of a small amount of a polyglycol derivative. A typical example is given below.

TABLE III

Example	Polyalkylene Glycol Derivative added	Cloud Point of Di-iso-octyl Azelate, ° F.	
		Containing 0.1% Water	Containing 0.2% Water
9	None	0	+45
10	5% C	−70	0
11	10% C		−75

Also, addition of 5 percent polyglycol B to di-2-ethylhexyl sebacate containing 0.06 percent of water by Karl Fischer analysis lowered the ester cloud point from −20° F. to below the pour point of the fluid. Storage tests of 72 hours duration at a −65° F. temperature with di-2-ethylhexyl adipate containing 0.09 percent water indicated that 10 percent of polypropylene oxide monobutyl ether of a viscosity of 525 Saybolt Universal seconds (SUS), 6.5 percent of the same type of polyglycol having a viscosity of 1145 Saybolt seconds or 6 percent of the same having a viscosity of 1715 Saybolt seconds, or 22.5 percent polypropoxy dibutyl ether of a viscosity of 130 Saybolt seconds, result in clear blends. This is to be contrasted with samples of the adipate alone or mixed with polymethylmethacrylate thickeners which become turbid after similar exposure.

Another advantage of mixtures of di-esters with polyoxyalkylene glycols is the marked improved-temperature-viscosity characteristics of the di-esters. This is shown in Table IV following, by the blends of Examples 12 to 18 inclusive, prepared for use at minimum temperatures and general operating characteristics of turbine engines.

TABLE IV

Examples 12 to 18

Example	Corrosion-inhibited Blend Containing 5% Tricresyl Phosphate and 0.5% Phenothiazine	Viscosity (cstks.)			Hardiman and Nissan V.I.
		210° F.	100° F.	−65° F.	
12	Di-2-ethylhexyl sebacate	3.35	13.3	12,600	143
13	Di-2-ethylhexyl adipate	2.40	8.45	6,650	130
14	Di-2-ethylhexyl adipate plus 5 percent of "A."	3.14	11.27		154
15	Di-2-ethylhexyl adipate plus 22.5 percent of "B."	3.01	11.10	12,400	149
16	Mixed alcohol pimelate	2.33	7.94		150
17	Mixed alcohol pimelate plus 6 percent of "A."	3.26	11.36	7,650	159
18	Mixed alcohol pimelate plus 25 percent of "B."	3.10	11.07	9,450	154

The foregoing additives in general gave better performance than "unblocked" polyglycols such as polypropylene glycol. Such compounds have applicability in particular cases. Typically the performance of polypropylene glycol appears in Table V.

TABLE V

Effect of polyglycol on cloud point of di(2-ethylhexyl) sebacate

Additive	Water Content of Diester	Cloud Point on Cooling (° F.)
None	0.03	−35
	0.05	−20
10% Polypropylene Glycol 425	0.03	Below −80
	0.05	Below −80

It is to be understood that the benefits obtained by the addition of polyoxyalkylene glycols to aliphatic di-ester fluids are realized in the presence of other agents which may be added to the base fluids to overcome other performance problems. The end use of these fluids, for example, hydraulic fluids for aircraft engines, may require the inclusion of other additives for control of oxidation, lubricity, corrosion and viscosity tailoring. Oxidation control additives generally consist of aromatic amines such as phenothiazine or substituted phenols, and sometimes may contain sulfur. Improved lubricity or load-carrying ability can be secured by the addition of organophosphate compounds of the type obtained by the reaction of inorganic phosphorus compounds with petroleum fractions (example—tricresylphosphate). Conventional corrosion problems are resolved through the selection of base fluid blends, together with proper choosing of additives for other purposes, as well as by the addition of specific corrosion inhibitors. Viscosity tailoring of fluid may be effected by the addition of selected polymers such as polymethylmethacrylate or siloxanes. Accordingly, various modifications and variations may be effected as regards these conventional additives without departing from the range of the invention or from the scope of the appended claims.

What is claimed is:

1. A lubricant fluid having improved viscometric stability and low temperature water tolerance consisting of 5 percent polyoxypropylene glycol monobutyl ether, 5 percent tri-cresyl phosphate, 0.5 percent phenothiazine, the balance di-2-ethylhexyl adipate, said mixture having a Hardiman and Nissan viscosity index of 154.

2. A lubricant fluid consisting of a mixture of di-2-ethylhexyl adipate plus 22½ percent of polyoxypropylene glycol dibutyl ether, 5 percent tri-cresyl phosphate and 0.5 percent of phenothiazine, said mixture having a viscosity of about 12,000 centistokes at −65° F. and a Hardiman and Nissan viscosity index of 149.

3. A lubricant fluid for gas turbine engines consisting of 6 percent polyoxypropylene glycol monobutyl ether, 5 percent tri-cresyl phosphate, 0.5 percent phenothiazine, the balance consisting of mixed alcohol pimelates, said mixture having a viscosity of about 7,600 centistokes at −65° F. and a Hardiman and Nissan viscosity index of about 159.

4. A lubricant fluid for gas turbine engines consisting of 80 percent di-2-ethylhexyl adipate and 20 percent of a polyoxypropylene glycol dibutyl ether having a viscosity of 130 Saybolt Universal seconds at 100° F.

5. A lubricant fluid for gas turbine engines consisting of 90 percent of di-2-ethylhexyl adipate and 10 percent of a butyl ethyl diether of a polyoxyalkylene glycol of a viscosity of 59 Saybolt Universal seconds at 100° F.

6. A lubricant and hydraulic fluid mixture having improved viscometric stability and low temperature water tolerance containing, in addition to conventional additives for the control of oxidation, lubricity, corrosion and viscosity, 20 percent of polyoxypropylene glycol di-butyl ether having a viscosity of 130 Saybolt Universal seconds at 100° F., the balance being di-2-ethylhexyl adipate.

7. A lubricant and hydraulic fluid mixture having improved viscometric stability and low temperature water tolerance containing in addition to conventional additives for the control of oxidation, lubricity, corrosion and viscosity, 10 percent of a butyl ethyl di-ether of a polyoxyalkylene glycol having a viscosity of 59 Saybolt Universal seconds at 100° F., the balance being di-2-ethylhexyl adipate.

8. A lubricant and hydraulic fluid having improved viscometric stability and low temperature water tolerance, consisting essentially of a mixture composed of at least one aliphatic diester selected from the group consisting of the higher alkyl adipates, sebacates, azelates and pimelates, and from 2 to 22½ percent of at least one high viscosity alkyl polyoxyalkylene glycol ether selected from the group consisting of lower alkyl mono- and di-ethers of polyoxypropylene and polyoxyethylene glycols, the viscosity of said ether ranging from about 59 Saybolt Universal seconds to about 3000 Saybolt Universal seconds at 100° F.

9. The fluid of claim 8 additionally characterized by the presence therein of conventional additives for the control of oxidation, lubricity, corrosion and viscosity.

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