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POLYESTERS OF BENZENE POLYCARBOXYLIC ACIDS WITH FLUORINATED ALKANOLS

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This invention relates to new polyesters of benzene polycarboxylic acids and particularly to highly fluorinated alkyl polyesters which are of value as lubricants and as fluids for transmitting power and heat, especially at high temperatures.

There is an increasing demand for stable lubricants and hydraulic fluids to meet the requirements of new military and industrial equipment. For example, the trend in the design of high speed aircraft and of engines capable of providing the power therefor necessitates the provision of lubricants and hydraulic fluids capable of withstanding the increased internal temperatures developed in the flight of the vehicle and in the operation of its power plants and also of performing their intended functions at these severe temperatures. It is desired that fluids designed for such uses be stable at and to function at temperatures of at least about 400° F. or higher, even as high as 600° F. Conventional fluids, such as the esterlubes and the petroleum oils, are unsatisfactory at temperatures much in excess of 300° F., primarily because they lack the requisite thermal and oxidative stability. Dibasic acid esters of fluoroalcohols as a class (disclosed by Faurote et al. in Ind. and Eng. Chem., vol. 48, No. 3, March 1956, pages 445–454) are now generally recognized as having better oxidation and thermal stability and lower flammability than the conventional alkyl esters of dibasic acids or the petroleum oils, and accordingly have been suggested as promising for a variety of high temperature applications. However, at high temperatures such as the 400–600° F. range, they are either too volatile for practical use in any but closed systems or have relatively poor viscosity-temperature relationships.

It is an object of this invention to provide a class of new polyesters of benzene polycarboxylic acids which have a beneficial combination of thermal, oxidation, volatility, and viscosity-temperature characteristics. Another object is to provide new polyesters of such character which are useful as lubricants and as fluids for transmitting power and heat over a wide range of temperatures, particularly at high temperatures. Further objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

The above and other objects are accomplished in accord with this invention which comprises a class of polyesters of benzene polycarboxylic acids each of which polyesters has the formula

$$C_6H_{6-m}[—CO_2—CH_2(CF_2CF_2)_nH]_m$$

wherein m represents an integer of from 3 to 4 and n represents an integer of from 1 to 5, particularly mixtures of such polyesters. Such polyesters may also be defined as neutral polyesters of a benzene polycarboxylic acid and one or more alcohols in which the benzene polycarboxylic acid contains 3 to 4 carboxylic acid groups and each of the alcohols is a member of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 5; the term "neutral" meaning that each carboxylic acid group of the polycarboxylic acid has been esterified with one of those alcohols.

It has been found that the new polyesters of this invention have high thermal and oxidation stability and low flammability, have low volatility at high temperatures up to at least 400° F., and have viscosity-temperature relationships which are surprisingly superior to such relationships of related materials. For example, the polyesters of this invention have relatively large positive viscosity indexes and relatively low ASTM slopes, which are highly desirable in lubricants to be used over a range of temperatures. Also, as a class, they have viscosities of at least about 1 centistoke at 500° F. and above, which are essential for practical efficiency as lubricants at those temperatures. Therefore, these new polyesters are particularly suitable and superior for use as lubricants under severe conditions, in open as well as closed systems, as for example for aircraft turbines or silicone-insulated electric motors and generators; as fluids for transmitting heat and power; and in other systems required to operate at high temperatures.

The new polyesters are conveniently obtained by esterifying the appropriate benzene polycarboxylic acid or a functional derivative thereof, such as an anhydride or acid chloride thereof, with the appropriate alcohol. The benzene carboxylic acids contain 3–4 carboxylic acid groups, i.e. they are the benzene tricarboxylic acids and the benzene tetracarboxylic acids, having the formula $C_6H_{6-m}(CO_2H)_m$ wherein m is an integer of from 3 to 4. Representative acids are trimellitic acid, trimesic acid, mellophanic acid, pyromellitic acid, and mixtures of two or more thereof, and the corresponding anhydrides and acid chlorides of those acids. The best and most preferred products are the pyromellitates (the neutral polyesters of pyromellitic acid), obtained from pyromellitic acid, its anhydride or its acid chloride.

The alcohols, employed for making the polyesters of this invention, are the polyfluoroalcohols having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n is an integer of from 1 to 5, preferably from 1 to 4. These polyfluoroalcohols are known as telomer alcohols and are readily prepared, as described by Robert M. Joyce, Jr. in Patent No. 2,559,628, from tetrafluoroethylene and methanol by a telomerization process which comprises heating a mixture of tetrafluoroethylene and methanol in the presence of a peroxy or an azo catalyst. This telomerization process produces a series of alcohols which contain at least one $—CF_2CF_2—$ unit per molecule of methanol, including the alcohols employed to prepare the polyesters of this invention. Mixtures of the desired telomer alcohols are readily and economically manufactured by the process of Joyce. The use of such mixtures of telomer alcohols in the preparation of the polyesters produces mixtures of polyesters which have particularly desirable advantageous properties, and such mixtures of polyesters constitute preferred embodiments of this invention. The telomer alcohols, employed in the making of the polyesters of this invention, include 1,1,3-trihydroperfluoropropyl alcohol (C_3), 1,1,5-trihydroperfluoropentyl alcohol (C_5), 1,1,7-trihydroperfluoroheptyl alcohol (C_7), 1,1,9-trihydroperfluorononyl alcohol (C_9), 1,1,11-trihydroperfluoroundecyl alcohol (C_{11}), and mixtures of any two or more thereof.

The polyesters of this invention may be prepared readily by heating the benzene polycarboxylic acid or its functional derivative, preferably an anhydride thereof, with at least a stoichiometric quantity of the telomer alcohol or mixture of telomer alcohols in the presence of an acid esterification catalyst, in the presence or absence of a solvent, and removing the water of reaction as formed. It is convenient to maintain the system at a temperature sufficiently high to vaporize the water under the prevailing conditions, e.g. as an azeotrope with the inert solvent or alcohol.

As in conventional esterification processes, using the azeotroping solvent technique, about a 10% excess of

telomer alcohol is employed and an inert solvent is chosen which is more volatile than any of the reactants, which is capable of being heated to a temperature sufficient to effect esterification, and which is capable of removing the water of reaction as by entrainment. In such processes, it is convenient to operate at the reflux temperature of the reaction mass (which temperature is determined primarily by the boiling point of the solvent), condensing the distilling vapors, then removing the water layer from the distillate and returning the organic phase to the reaction vessel. Benzene, toluene, xylene, chlorobenzene, ortho-dichlorobenzene, excess telomer alcohol, and mixtures are suitable solvents. Reaction temperatures which are higher than normally obtainable with, for example benzene (boiling point 80° C.), may be attained by operating the system under pressure, or by using a solvent which boils higher than benzene but lower than the alcohol. Conversely, temperatures, lower than the reflux temperatures at atmospheric pressure, can be attained by operating under reduced pressure. Reaction temperatures of up to about 200° C. are practical.

The C_3 telomer alcohol has a normal boiling point of 108° C. and, when this alcohol is involved in the esterification, benzene and benzene-toluene mixtures which are appreciably lower boiling are practical solvents. Toluene and xylene are suitably low-boiling solvents for the esterification of the higher boiling telomer alcohols, such as the C_5 telomer alcohol (B.P. 140–141° C.), the C_7 telomer alcohol (B.P. 171–172° C.) and the still higher boiling C_9 and C_{11} telomer alcohols, which boil at 156–157° C. and 180–181° C., respectively, at 200 mm. of Hg pressure.

The preferred process involves direct esterification in the absence of solvent. It has been found that a marked improvement in the rate of esterification is achieved simply on heating the alcohol (usually in about 50 mole percent excess) with the anhydride (or acid) in presence of the esterification catalyst at about 100–200° C. and removing the water of reaction as its azeotrope with the telomer alcohol. It is preferred, but it is not necessary, that the alcohol reflux; the water of reaction can be swept out of the system in a stream of an inert gas such as nitrogen or carbon dioxide. Conveniently, however, the reaction mass is heated to reflux; normally this temperature of the reaction mass will be about 10° C. higher than the boiling point of alcohol. Thus, at atmospheric pressure, the lower temperature limit will be about 120° C. for the C_3 alcohol. Higher and lower reflux temperatures than those obtainable at atmospheric pressure are obtained by operating at elevated and reduced pressures, as the case may be. For example, with the C_{11} telomer alcohol, a temperature of about 180° C. may be achieved at about 200 mm. of Hg pressure. The preferred range is about 140–180° C. at a pressure in accord with the vapor pressure-temperature relationships of the alcohols employed.

The water of reaction distills from the reaction mass along with telomer alcohol and forms the upper layer of the distillate; the telomer alcohol layer is returned to the reaction vessel. Preferably, the distillate is chilled (e.g. in an ice bath) to minimize the solubility of water in the telomer alcohol before the layers are separated.

When the reaction is complete, the reaction mass is diluted with a water-immiscible, volatile solvent for the polyester, such as benzene or toluene. The diluted reaction mixture, or the mixture obtained by carrying out the reaction in a solvent, is treated to remove acidic materials, solvent and excess alcohol, when present, to obtain a residue comprising the polyester or mixture of polyesters. Since the polyesters are too high boiling for convenient and economical recovery and purification by distillation methods, it is preferred to employ non-distillative techniques such as solvent extraction, washing, adsorption on solid substrates, and the like to obtain substantially pure and serviceable esters. Preferably, the reaction mass is cooled (for convenience in handling) to about room temperature and washed with aqueous alkali (caustic or carbonate) to remove such soluble acidic materials as catalyst and partially esterified acids. Volatile components, such as solvent, excess alcohol, and esterified catalyst (if formed), are stripped from the reaction mass, as by vacuum distillation in a stream of nitrogen, and the residual product further purified by treatment while hot with decolorizing agents and/or adsorbents, e.g. activated carbons and aluminas, sometimes in conjunction with a weak base, e.g. basic metal carbonates, and filtered hot. Alternately, if the product is highly viscous or solid at ambient temperatures, the reaction mass may be treated with decolorizing agents and/or adsorbents after it has been washed with alkali and before the volatile components, such as solvent and excess alcohol, are stripped therefrom.

The products obtained are normally colorless to light yellow clear oils or solids, depending on the composition of the benzenepolycarboxylic acid and the telomer alcohol starting materials. Their identification as esters having the defined structure is established by the method of preparation and by elemental and chemical analyses.

The conventional acid esterification catalysts may be used in the esterification process, such as sulfuric acid, fluorosulfonic acids, p-toluenesulfonic acid, perfluorobutyric acid, and the like.

In the preferred embodiment of the invention, a mixture of two or more telomer alcohols having the above defined structure is esterified with a benzene tri- or tetracarboxylic acid, preferably pyromellitic acid, to produce a mixture of mixed esters. Preferably, in the telomer alcohol mixture, the minor component will comprise at least about 20–25 mole percent of the total. Examples of such mixtures are: the approximately equimolar mixture of 1,1,3-trihydroperfluoropropyl alcohol (C_3), 1,1,5-trihydroperfluoropentyl alcohol (C_5), 1,1,7-trihydroperfluoroheptyl alcohol (C_7), and 1,1,9-trihydroperfluorononyl alcohol (C_9); the approximately equimolar mixture of the C_3 and C_5 alcohols; and the approximately equimolar mixture of the C_5 and C_7 alcohols. In the esterification process, the mixture of telomer alcohols may be added together all at once, or the components of the chosen alcohol mixture may be added singly or, in different combinations with each other, during the course of the reaction.

The use of telomer alcohol mixtures as starting materials is preferred, partly because the step of isolating the individual alcohols from the mixtures produced in the telomerization process is thus avoided, but mainly because the mixed esters, e.g. the pyromellitates, produced from them are especially valuable in having greatly extended liquid ranges. Their pour points usually are below ambient temperatures and the freezing point of water, while their boiling ranges are well over 700° F. Such fluid mixtures, in having the aforementioned excellent thermal and oxidative stability, the low volatility at 400° F., and the favorable viscosity-temperature relationships that are characteristic of the esters of this invention, are adapted for general use as lubricants and fluids for transmitting heat and power, particularly where required to function as such at high temperatures.

When fluidity at low temperatures is not essential, the relatively higher melting members of the present class of esters are also useful as fluids at higher temperatures. For example, they may be used as engine lubricants that may be maintained fluid and mobile by auxiliary heating means to allow for normal circulation and for movement of lubricating surfaces without undue power requirement at the start of engine operation.

In order to more clearly illustrate this invention, preferred modes of making the polyesters thereof, and the advantages thereof, the following examples are given

in which the proportions are by weight except where specifically indicated otherwise.

EXAMPLE 1

A mixture of 109 parts (0.5 mole) of pyromellitic dianhydride, 510 parts (2.2 moles) of 1,1,5-trihydroperfluoropentyl alcohol, 5.5 parts (0.056 mole) of sulfuric acid (specific gravity 1.84) and 260 parts of toluene was refluxed for 48 hours. The water formed during this period was separated from the distillate and the toluene returned to the reactor. A total of 15.5 parts of water (theory 18.0 parts) was collected. The oil, after cooling to room temperature, was washed with three 1000 part portions of 1% potassium hydroxide and distilled to 140° C. at 10 mm. of mercury. A mixture of 10 parts of activated alumina (8–14 mesh) and 5 parts of decolorizing carbon was added to the oil which was then heated in a distillation apparatus to 170° C. at about 1 mm. of mercury for 2 hours to remove volatiles, and filtered hot to yield 307 parts of a nil acid number pale yellow oil which crystallized to a solid melting at 38–39° C. (100–103° F.).

The product is high boiling and has low volatility at 400° F. In the 2 hour test described below, the weight loss of the sample is less than 3%.

It exhibits the following viscosity-temperature relationships:

Viscosity at 210° F., cs	27.2
Viscosity at ~ 100° F. (M.P.), cs	652
Viscosity index (ASTM–D–567)	60
ASTM slope (~ 100–210° F.)	0.73

This material has a viscosity of 1 cs. at an estimated temperature of about 525° F.

The volatility test data are obtained for the above and other compounds of this invention as follows: Aluminum foil dishes, 1½" in diameter and ⅜" deep, are weighed to 0.1 mg., then each is charged with about 1 gm. of the sample to be tested and reweighed to 0.1 mg. The charged dishes are then placed on a 3" by 6" copper plate equipped with a thermocouple and resting on a variac-controlled hot plate. The temperature of the copper plate is adjusted to 400° F. by means of the variac-controlled hot plate and the dishes containing the test samples are allowed to remain on the 400° F. copper plate for 2 hours. This test is carried out in a well-ventilated hood to remove any noxious and toxic fumes and to provide a circulating atmosphere above the sample surface. At the end of the two-hour test period, the test dishes are removed and are reweighed as before to determine the sample weight loss.

EXAMPLE 2

A mixture of 54.5 parts (0.25 mole) of pyromellitic dianhydride, 365 parts (1.1 mole) of 1,1,7-trihydroperfluoroheptyl alcohol, 5 parts (0.05 mole) of p-toluenesulfonic acid, and about 350 parts of xylene were refluxed with continuous separation of water from the condensate, the xylene being returned to the kettle. After about 125 hours, 9 parts of water had been removed. The reaction mixture was cooled and washed at room temperature with three 1000 part portions of 1% aqueous potassium hydroxide. The oil layer was distilled at still pot temperatures of up to about 120° C. at 25 mm. of mercury pressure to remove the solvent and some of the excess telomer alcohol. The pot residue was treated with 5 parts of decolorizing carbon and 10 parts of activated alumina (8–14 mesh) and, after heating in a distillation apparatus to 130° C. at less than 1 mm. of mercury for three hours, the mixture was filtered hot. The pale yellow product (250 parts having a nil acid number) solidified, melting at 53–55° C. (128–131° F.). This relatively low melting solid is high boiling and substantially involatile at 400° F. In the 400° F. two hour volatility test, described in Example 1, its weight loss is 0.5 weight percent. It has a viscosity of 40.2 centistokes at 210° F.

EXAMPLE 3

The procedure of Example 1 was repeated except that the C_5 fluoroalcohol was replaced by an equimolar quantity of 1,1,3-trihydroperfluoropropyl alcohol and the benzene solvent was replaced by a 1:1 mixture of benzene and toluene. The tetra-(1,1,3-trihydroperfluoropropyl) pyromellitate was obtained as a pale yellow solid melting at 77–77.5° C. (161–162° F.) after recrystallization from ethyl acetate-petroleum ether. Its viscosity at 210° F. is 34.7 cs.; at 250° F., 15.4 cs.; at 500° F. (estimated), its viscosity is at least 1 cs. In the 400° F. two hour volatility test of Example 1, the compound shows a weight loss of less than 5%.

EXAMPLE 4

170 grams (1.3 moles) of 1,1,3-trihydroperfluoropropyl alcohol in 200 ml. of pyridine was added in 2 hours to 100 gm. (0.3 mole) of pyromellitoyl chloride, under a sweep of nitrogen, at 65–70° C., and the reaction mass stirred two additional hours at 70° C., and overnight at room temperature. The liquid mixture was drowned in water (1 liter) and the organic product taken up in toluene (200 ml.). The toluene layer was worked up in the usual way: solvent-stripped; treated with decolorizing carbon (2 gm.) and activated alumina (5 gm.) and heated at 180–185° C. at 1.2 mm. Hg in a stream of nitrogen to remove volatile materials; and filtered hot to yield the tetra-(1,1,3-trihydroperfluoropropyl) pyromellitate (M.P. 76–77° C.), but in lower yield than in Example 3.

EXAMPLE 5

A mixture of 48 parts (0.25 mole) of trimellitic anhydride (which contains a free carboxylic acid group), 274 parts (0.825 mole) of 1,1,7-trihydroperfluoroheptyl alcohol, 175 parts of xylene plus 50 parts of toluene, 5 parts (0.05 mole) of p-toluene sulfonic acid, and about 4 parts of concentrated sulfuric acid was refluxed for 91 hours, at the end of which time the theoretical quantity of water had been collected. The mixture, as in the previous examples, was washed with three 500 part portions of 1% potassium hydroxide, and the oil layer was distilled to a pot temperature of 140° C. at 10 mm. of mercury. After the addition of 5 parts of decolorizing carbon and 10 parts of alumina, the mixture was pumped at 160–170° C. at 1 mm. of mercury for 1 hour with a slow stream of nitrogen bubbling through it, then filtered hot to give 183 parts of a dark yellow viscous oil having the following properties:

Viscosity at 210° F., cs	17.3
Viscosity at 100° F., cs	369
Viscosity index (ASTM–D–567)	25
ASTM slope	0.790
Pour point, ° F	0
Volatility, percent loss at 400° F. in 2 hours	[1] 3.7

[1] By the test described in Example 1.

Its viscosity is about 1 cs. at about 480° F. (estimated) and 10,000 cs. at about 35° F. (estimated).

EXAMPLE 6

A mixture of 109 parts (0.5 mole) of pyromellitic dianhydride, 145 parts (1.1 mole) of 1,1,3-trihydroperfluoropropyl alcohol, 255 parts (1.1 mole) of 1,1,5-trihydroperfluoropentyl alcohol, 5.5 parts (0.056 mole) of sulfuric acid (specific gravity 1.84) and about 260 parts of benzene was refluxed for 236 hours, during which time about 17 parts of water (theory=18 parts) was collected. The mixture at room temperature was washed three times with 1000 parts each of 1% aqueous potassium hydroxide.

To the separated oil layer, there was added 5 parts of anhydrous potassium carbonate, 10 parts of decolorizing carbon, and 20 parts of activated alumina (8–14 mesh). The mixture was distilled to a still pot temperature of 170° C. at about 1 mm. of mercury and held at these conditions for 1 hour, and filtered hot. A pale yellow oil, 318 parts, was obtained having a microboiling point of about 725° F. This high boiling oil is further characterized by the following properties:

Viscosity at 210° F., centistokes	30
Viscosity at 100° F., centistokes	806
Viscosity index (ASTM–D–567)	51
ASTM slope, 100–210° F	0.74
Estimated temp. (° F.) at which viscosity is 1 cs	535
Estimated temp. (° F.) at which viscosity is 10,000 cs	50
Pour point, ° F	14
Volatility, percent loss at 400° F. in 2 hrs	[1] 3.1

[1] By the test described in Example 1.

EXAMPLE 7

The procedure of Example 2 was repeated, using as the fluoroalcohol an equimolar mixture of 1,1,5-trihyproperfluoropentyl alcohol and 1,1,7-trihydroperfluoroheptyl alcohol. The corresponding mixed pyromellitate esters were obtained in 70% yield, as a light yellow viscous oil having the properties tabulated below:

Viscosity at 210° F., cs	30.8
Viscosity at 100° F., cs	723
Viscosity index (ASTM–D–567)	67
ASTM slope, 100–210° F	0.713
Estimated temp. (° F.) at which viscosity is 1 cs	550
Estimated temp. (° F.) at which viscosity is 10,000 cs	50
Pour point, ° F	16
Volatility, percent loss at 400° F. in 2 hrs	[1] 1.0

[1] By the test described in Example 1.

EXAMPLE 8

A mixture, consisting of pyromellitic anhydride (39.3 lbs., 0.18 mole), C_5 telomer alcohol (125.3 lbs., 0.54 mole), C_7 telomer alcohol (179.3 lbs., 0.54 mole), and sulfuric acid (d. 1.84, 1.2 lbs.), was heated to reflux at a pot temperature of 150° C. The two-phase distillate was processed continually by cooling in an ice bath, separating the layers and returning the lower (alcohol) layer to the reaction vessel. After 20 hours, about 95% of the theoretical quantity of water had been removed and, after 24 hours, water no longer appeared in the distillate. The pot temperature at this stage was 170° C.

The mass was allowed to cool. Benzene (45 lbs.) was added and the whole washed with about ½ volume each of water (twice), dilute aqueous carbonate (twice), and water (twice). The benzene was distilled off, and decolorizing carbon (2.5 lbs.) and alumina (5 lbs.) were added and the mass heated to and held at 140° C. at 10 mm. of Hg pressure in a slow stream of nitrogen in a simple distillation apparatus until telomer alcohol no longer came over (20 hours). The mixture was filtered hot and the filtrate (product) recovered in at least 85% yield. The product corresponded to that of Example 7.

EXAMPLE 9

The procedure of Example 6 was repeated except that the mixture of alcohols employed therein was replaced by an equimolar quantity of a mixture consisting of equal moles of 1,1,3-trihydroperfluoropropyl alcohol, 1,1,5-trihydroperfluoropentyl alcohol, 1,1,7-trihydroperfluoroheptyl alcohol and 1,1,9-trihydroperfluorononyl alcohol. The corresponding mixed pyromellitate was obtained in about 72% yield as a light yellow viscous oil having the properties tabulated below:

Viscosity at 210° F., cs	60.7
Viscosity at 100° F., cs	948
Viscosity index (ASTM–D–567)	114
ASTM slope, 100–210° F	0.56
Estimated temp. (° F.) at which viscosity is 1 cs	640
Estimated temp. (° F.) at which viscosity is 10,000 cs	45
Pour point, ° F	23
Volatility, percent loss at 400° F. in 2 hrs	[1] 2.0

[1] By the test described in Example 1.

In general, the polyesters of this invention are far less volatile than the corresponding fluoroalcohol esters of such dibasic acids as phthalic, 3-methylglutaric and pinic acids, all of which suffer weight losses in the above 400° F. volatility test many times that of the subject esters. For example, the weight loss of di(1,1,7-trihydroperfluoroheptyl)phthalate in this test is 86%, that of di(1,1,7-trihydroperfluoroheptyl)3-methylglutarate is about 81%, and that of the di(1,1,7-trihydroperfluoroheptyl)pinates is 24–95%. The subject esters as a class have viscosities of at least about 1 centistoke at 500° F. In contrast, the corresponding telomer alcohol esters of phthalic acid and of the aliphatic dibasic acids at 400° F. have viscosities of about 1 centistoke or less, as reported on page 450 of the aforementioned article by Faurote et al. The significance of these results is that a viscosity of about 1 centistoke can be regarded as the lowest practical viscosity a lubricant may have and still satisfactorily function as a lubricant. Futhermore, it should be noted that di(1,1,5-trihydroperfluoropentyl)phthalate is reported in the above article by Faurote et al. to have a large negative viscosity index (−64) and a relatively high slope of 0.91. The di-(1,1,7-trihydroperfluoroheptyl)phthalate and the corresponding isophthalate also have been found to have large negative viscosity indexes, i.e., −55 and −29, respectively, with slopes (100–200° F.) of 0.91 and 0.89, respectively. In view of these data, the positive viscosity indexes and the relatively low slopes of the polyesters of this invention are unexpected and surprising.

The suitability of the subject esters as lubricants is further illustrated by the results of the lubricity test of Example 10.

EXAMPLE 10

Lubricity characteristics

The load carrying ability of candidate stable lubricants is indicated by the "rapid Falex test" (E. G. Ellis, Lubricant Testing, 1953, p. 153). Essentially, the test involves the failure of an oil to carry a load as evidenced by the seizure of the test pin and bushings or a sudden increase in torque reading. The procedure involved is as follows: The sample reservoir of the Falex test machine is filled with about 50 ml. of the fluid to be tested and placed in position such that the fluid covers the test pieces. The jaw-load is adjusted to 250 pounds and the torque gauge linkage adjusted to 0. The machine is started and, following a 3-minute run-in period during which time the load is maintained at constant load, the automatic loading device is engaged. The load at which the torque reading shows a sudden increase and/or seizure occurs is recorded as the maximum load held. The behavior in this test of the tetra (mixed 1,1,5-trihydroperfluoropentyl and 1,1,7-trihydroperfluoroheptyl) pyromellitate of Example 7 and of di(2-ethylhexyl)sebacate as the comparison lubricant is given below:

FALEX TEST DATA

Compound Tested	Max. Jaw-Load at Seizure (lbs.)
The mixed C_5:C_7 pyromellitate of Example 7	>4,500
di(2-ethylhexyl)sebacate	1,500

The excellent performance of the above illustrative compound of this invention in this test is representative of that of the other novel esters of this invention.

EXAMPLE 11

Oxidative stability

The oxidative stability of the subject esters is measured by the following tests at 500° F. and 570° F.: In the 500° F. test: 10–15 ml. of the test sample and a freshly cleaned strip of copper are placed in a glass reaction cell equipped with a glass reflux condenser. The entire assembly is then placed in a metal bath heated to, and maintained by thermostatic controls at 500° F. A continuous flow of dry air is passed via a flow meter at a rate of 25 ml./min. through the heated test sample for 24 hours. At the end of this period, the cell-condenser assembly is removed from the metal bath and allowed to cool. The test sample is then tested for changes in general appearance and in viscosity. The weight loss of the cell is also determined and expressed as grams per milliliter of charge. The following results were obtained, employing the mixed tetra (1,1,3-trihydroperfluoropropyl- and 1,1,5-trihydroperfluoropentyl) pyromellitate of Example 6 and the tri-(1,1,7-trihydroperfluoroheptyl) trimellitate of Example 5. Comparison is made with di(1,1,7-trihydroperfluoroheptyl) 3-methylglutarate.

24 HR. 500° F. OXIDATION TEST

Compound	Fluid Appearance	Percent Change in Viscosity		Cell Wt. Loss, g./ml.
		100° F.	210° F.	
C_3:C_5 pyromellitate of Example 6.	Clear light amber.	nil	−4.1	nil
C_7 3-methylglutarate	Dark brown	8.7	(1)	0.20
C_7 trimellitate of Example 5.	do	2.2	4.7	0.03

[1] Not determined.

From this data, the excellent oxidative stability of the subject pyromellitate is apparent. That of the trimellitate is less good but is superior to that of the 3-methylglutarate. The other esters of this invention are essentially as inert as the above illustrative esters.

In the 570° F. test, a stainless steel cell is employed, and the procedure is the same except that the test sample is held at the stated temperature for 16 hours while a stream of dry air is passed through it at a rate of about 90 ml./min. After being held under these conditions, tetra(1,1,7-trihydroperfluoroheptyl) pyromellitate was found to be essentially unchanged in all its properties. In contrast, when di(1,1,7-trihydroperfluoroheptyl) 3-methylglutarate and di(2-ethylhexyl)sebacate are subjected to this test, the former blackens and deposits a considerable amount of sludge, and the latter is substantially completely decomposed.

It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not limited to the specific embodiments disclosed therein. On the other hand, it will be apparent to those skilled in the art that polyesters derived from other benzene tri- and tetracarboxylic acids and mixtures thereof and from other telomer alcohols and other mixtures of the telomer alcohols, in varying proportions, all within the limits set forth in the general disclosure, can be made without departing from the spirit and scope of this invention. Likewise, the methods of making the polyesters, including the conditions, catalysts, solvents, and the like, may be widely varied without departing from this invention.

From the preceding description, examples and tests, it will be readily apparent that this invention provides a class of new polyesters which have a combination of very valuable and unusual beneficial properties whereby they are outstandingly useful for many purposes and under a wide range of conditions, particularly under high temperature conditions. In addition, they are readily prepared in high yields by means of simple and economical processes. Thus, it is obvious that this invention constitutes a valuable advance in, and contribution to the art.

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

1. A polyester of a benzene polycarboxylic acid having the formula

$$C_6H_{6-m}[—CO_2—CH_2(CF_2CF_2)_nH]_m$$

wherein m represents an integer of from 3 to 4 and n represents an integer of from 1 to 5.

2. A polyester of a benzene tetracarboxylic acid having the formula

$$C_6H_2[—CO_2—CH_2(CF_2CF_2)_nH]_4$$

wherein n represents an integer of from 1 to 5.

3. A polyester of pyromellitic acid having the formula

$$C_6H_2[—CO_2—CH_2(CF_2CF_2)_nH]_4$$

wherein n represents an integer of from 1 to 5.

4. A polyester of pyromellitic acid having the formula

$$C_6H_2[—CO_2—CH_2(CF_2CF_2)_nH]_4$$

wherein n represents an integer of from 1 to 4.

5. A mixture of polyesters each of which has the formula

$$C_6H_{6-m}[—CO_2—CH_2(CF_2CF_2)_nH]_m$$

wherein C_6H_6 represents a benzene ring, m represents an integer of from 3 to 4, and n represents an integer of from 1 to 5.

6. A mixture of neutral polyesters of a benzene polycarboxylic acid and a mixture of alcohols, in which the benzene polycarboxylic acid contains 3–4 carboxylic acid groups and each of the alcohols is a member of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 5.

7. A mixture of neutral polyesters of a benzene polycarboxylic acid and a mixture of alcohols, in which the benzene polycarboxylic acid contains 3–4 carboxylic acid groups and each of the alcohols is a member of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 4.

8. A mixture of neutral polyesters of a benzene tetracarboxylic acid and a mixture of alcohols of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 5.

9. A mixture of neutral polyesters of pyromellitic acid and a mixture of alcohols of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 5.

10. A mixture of neutral polyesters of pyromellitic acid and a mixture of alcohols of the class having the formula $H(CF_2CF_2)_nCH_2OH$ wherein n represents an integer of from 1 to 4.

11. A mixture of neutral polyesters of pyromellitic acid and a substantially equimolar mixture of 1,1,5-trihydroperfluoropentyl alcohol and 1,1,7-trihydroperfluoroheptyl alcohol.

12. A mixture of neutral polyesters of pyromellitic acid and a substantially equimolar mixture of 1,1,3-trihydroperfluoropropyl alcohol and 1,1,5-trihydroperfluoropentyl alcohol.

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