United States Patent Office 3,148,147 Patented Sept. 8, 1964

3,148,147
2,2-DIALKYL-1,3-PROPANEDIOL DIESTERS AS FUNCTIONAL FLUIDS

Alan Bell and Gerald R. Lappin, Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Jan. 31, 1961, Ser. No. 86,008
18 Claims. (Cl. 252—47.5)

This invention relates to new and improved synthetic ester lubricants and functional fluids and is particularly concerned with diesters of 2,2-dialkyl-1,3-propanediols wherein one of the alkyl radicals contains two to four carbon atoms and the other alkyl radical contains from two carbon atoms up to four or more in some instances.

This application is indirectly related to our prior application Serial No. 408,016 which is now U.S. Patent 2,798,083, and is a continuation-in-part of our application Serial No. 491,766, filed March 2, 1955, which has been abandoned in favor of the present application now covering certain especially preferred and unobvious embodiments. Although Serial No. 408,016 and Serial No. 491,766 were related as continuations-in-part, the present application is not directly based on anything disclosed in Serial No. 408,016.

It is an object of this invention to provide new synthetic ester lubricants which are surprisingly free of many of the disadvantages inherent in hydrocarbon lubricating oils and which show low changes in viscosity with changing temperature, low pour points, high oxidative stability, low volatility, and other advantageous properties.

Another object of this invention is to provide an improved class of new synthetic ester lubricants particularly adapted for use in applications wherein conventional hydrocarbon lubricants are unsuitable.

Another object of the invention is to provide new acyl diesters of 2,2-dialkyl-1,3-propanediols wherein the alkyl groups contain 2–4 or more carbon atoms, which diesters find particular utility as synthetic lubricants and as functional fluids in hydraulic systems and the like where high temperature oxidative stability is important.

Other objects will be apparent from the description and claims which follow.

The hydrocarbon lubricating oils are widely used as functional fluids in various apparatus but they suffer from certain disadvantages which limit their use for certain applications. In particular, hydrocarbon oils undergo marked viscosity changes with changes in temperature and have relatively high pour points when they have an acceptable viscosity at high temperatures. Furthermore, the hydrocarbon oils suffer some oxidation or other thermal decomposition at high temperatures. When hydrocarbon lubricating oils having a low pour point are used, they usually contain a considerable amount of volatile material which is lost at high temperatures with a consequent deleterious effect on the lubricating power of the oil.

Because of these inherent disadvantages, the hydrocarbon lubricating oils are not suitable for use in such critical applications as lubrication of turbo-jet aircraft engines and controls or instruments in multi-mach aircraft. In recent years, certain synthetic lubricants of the ester type have been proposed to overcome some of these disadvantages. A particularly useful class of esters are the diesters of certain substituted propanediols as disclosed in the above-mentioned application Serial No. 408,016, filed February 3, 1954, now U.S. Patent No. 2,798,083, of which the application Serial No. 491,766, now abandoned, was a continuation-in-part and likewise the present application is a continuation-in-part. The synthetic diesters disclosed in the original parent application are alkyl or alkoxyalkyl diesters of 2,2-dimethyl propanediols. The synthetic ester lubricants of the intermediate application were alkyl diesters of 2,2-dialkyl propanediols wherein one of the alkyl groups contains 1–4 carbon atoms and the other alkyl group contains 2–4 carbon atoms. The present application is limited to especially unobvious embodiments wherein the alkyl groups contain 2–4 carbon atoms.

A great deal has appeared in the literature in recent years concerning the effects of variations of chain length and chain branching upon the physical properties of synthetic ester lubricants. Thus, Industrial and Engineering Chemistry in volume 42 on pages 2415, 2434, and 2444 as well as elsewhere has set forth certain principles with regard to such synthetic ester lubricants. In volume 45, Industrial and Engineering Chemistry, on pages 1766–1775 additional observations have been set forth. McTurk under the title of "Synthetic Lubricants" has set forth observations concerning such synthetic ester lubricants in Wright Air Development Center Technical Report 53–88 dated October of 1953. In Naval Research Laboratory Report 4066, Cohen et al. in December of 1952 have set forth observations concerning such lubricants. For example, Cohen et al. state on page 9 that "it is notable that plots of viscosity vs. temperature on the ASTM chart are linear over the liquid range investigated for the majority of the diesters." Cohen et al. on page 2 state "the addition of side chains lowers the freezing point." According to Industrial and Engineering Chemistry, volume 42 on page 2415, "increasing the chain length increases the viscosity, raises the freezing point, and improves the viscosity-temperature characteristics as evidenced by higher viscosity indexes and lower ASTM slopes." McTurk indicates that "the addition of side chains increases the viscosity, lowers the freezing point, and has an adverse effect on the viscosity index and ASTM slope."

Industrial and Engineering Chemistry, volume 45 in Table IV, discloses 2-methyl-1,3-pentanediol dinonanoate which can also be called 1-ethyl-2-methyl-1,3-propanediol dipelargonate having a viscosity of 2.72 at 210° F., 10.0 at 100° F. and a pour point of 0. Although it would appear from some of the prior art that decreasing the chain length may effect a desirable lowering of the pour point and an undesirable decreasing of the viscosity, it would also appear that the unwanted lowering of the viscosity might be avoided by adding additional branching such as on the glycol radical whereby the addition of another methyl radical would increase the viscosity and at the same time lower the pour point. But a serious question would remain as to what effect this might have on the viscosity index and ASTM slope since McTurk indicates that this would be adversely affected. It would seem that an acid having a greater number of carbon atoms than nonanoic acid (pelargonic acid) could be used to compensate somewhat for the adverse effects of chain branching on the viscosity temperature characteristics. However, increasing the chain length does increase the freezing point as generally indicated by volume 42 of Industrial and Engineering Chemistry whereas chain branching lowers the freezing point as explained by McTurk to be the general rule. Thus, the conflicting effects of increasing chain length and increasing branching on the freezing point would be quite unpredictable. The freezing point is directly related to the pour point. It should be as low as possible.

Moreover, it is uncertain as to the effects of varia-

tions in chain length and chain branching on the stability of the synthetic ester lubricants at elevated temperatures. The trend and design of jet engines is toward higher and higher bearing temperatures. Previously reasonable stability at 425° F. was considered a sufficient degree of stability for a jet engine lubricant. However, more stringent military requirements as well as requirements for other usage have lead to conducting tests at temperatures in the range of 500°–550° F. Very few esters remain fluid for any appreciable time in the presence of air at 500° F. even when protected by an antioxidant. For example, 2-methyl-3-ethyl-1,3-propanediol diesters which are mentioned in the McTurk reference cited above have viscosities which increase by much higher orders of magnitude when subjected to high temperature oxidative conditions than do corresponding diesters of 2-methyl-2-ethyl-1,3-propanediol.

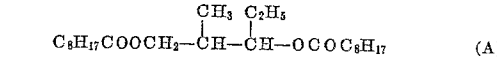
Thus, very few esters remain fluid for any appreciable time in the presence of air at 500° F. even when they are very closely related structurally to the esters of the present invention including various isomers and homologs of the esters of the present invention. The esters of the present invention do remain usable fluids for an advantageously long period of time at temperatures as high as 500° F. or higher under oxidative conditions. Moreover, the oxidative stability of the esters of the present invention is unexpectedly and unexplainably much greater than the corresponding esters of 2-methyl-2-alkyl-1,3-propane diols. For example, in an oxidation test at 500° F. 2-methyl-2-ethyl-1,3-propanediol dinonanoate was oxidized to a grease while 2,2-diethyl-1,3-propanediol dinonanoate remained a usable lubricating oil. Thus of the genus covered by the parent application, the species covered by the present patent application is unobviously superior to other species of the genus covered by the parent application.

Another unobvious aspect of the present invention is that the novel ester lubricants show oxidative stability at lower temperatures which is merely of the same general order of magnitude as the closely related isomers and homologs not being contemplated by this invention, and yet at the higher temperatures the differences in oxidative stability become unexpectedly large. From this data it appears that high oxidative stability at elevated temperatures such as 500° F. depends upon having both of the 2-alkyl groups of the 1,3-propanediol portion of the diester larger than methyl. No reasons based on any known theoretical grounds explain why such structures have such greatly enhanced oxidative stability at high temperatures.

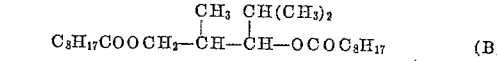
As previously pointed out, this invention provides new snythetic ester lubricants which are surprisingly free of many of the disadvantages inherent in hydrocarbon lubricating oils and which show low changes in viscosity with changing temperature, low pour points, high oxidative stability, low volatility, and other advantageous properties. Moreover, this invention provides an improved class of new synthetic ester lubricants particularly adapted for use in applications wherein conventional hydrocarbon lubricants are unsuitable. In addition, this invention provides new acyl diesters of 2,2-dialkyl-1,3-propanediols wherein the alkyl groups contain 2–4 carbon atoms, which diesters find particular utility as synthetic lubricants and as functional fluids in hydraulic systems, heat exchangers and the like where high temperature oxidative stability is important. Many governmental and commercial specifications have been proposed or prescribed for such functional fluids. However, emphasis should not be placed on meeting any particular specification. A few years ago, the important specification to meet was Mil–L–7808C which had no requirements as to high temperature oxidative stability but did have rather specific low- and high-temperature viscosity requirements. Present target specifications are much less specific as to viscosity requirements but do require high temperature oxidative stability combined with fluidity at −65° F.

Hence, it was quite unexpected to find that the esters of this invention have unexpectedly low viscosity at −65° F. For example, the Cohen reference cited states that temperature-viscosity plots for diesters are essentially linear. Applying thus to 2-butyl-2-ethyl-1,3propanediol dinonanoate, for example, leads to a predicted viscosity at −65° F. of about 29,000 cs. based on the measured viscosities at 100° F. and 210° F. The measured viscosity at −65° is only 15,553 cs. This is a large and unexpected deviation from linearity. If the predicted value had been accepted it would have been considered that this ester would be too viscous for use under present specifications. Similar deviations from predicted values exist for the other esters of this invention. In fact, this unexpected property may be as important as the high temperature oxidative stability in some practical applications.

With respect to the unobviousness of this invention it is to be noted that the following molecular structures are thermally unstable:



(A)

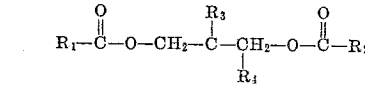


(B)

As an example of stability characteristics the following data is provided:

Property	2,2,4-trimethyl-1,3-pentanediol dinonanoate	2,2-diethyl-1,3-propanediol dinonanoate
Viscosity:		
110° F.	3.05 cs.	2.94 cs.
100° F.	11.76 cs.	11.46 cs.
−65° F.	6827 cs.	7593 cs.
Pour point	<−65° F.	<−55° F.
Thermal stability under nitrogen, 575° F.:		
Viscosity change	−40%	+1.1%.
Acid number increase	122	1.03.
Appearance	Dark brown, sludge.	Clear, light amber.
Oxidation stability (20 hrs. at 500° F. and 5 l. air per hr.) (see Table 3 for abbreviations)—Viscosity increase:		
1% PANA+1% DPA	Thick grease	302%.
1% phenothiazine	1655%	289%.

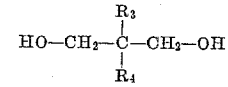
The above-mentioned and other objects are attained by means of this invention as described in detail hereinafter with particular reference to certain preferred embodiments thereof. The compounds embodying the invention and useful as synthetic lubricants are acyl diesters of the formula:



Compound I

wherein R_1 and R_2 are alkyl groups containing 4–12 carbon atoms, and preferably 6 to 11 carbon atoms, and R_3 and R_4 are alkyl groups containing 2–4 carbon atoms. R_1 and R_2 can be either straight or branched-chain alkyl groups, and can be the same or different groups as desired. R_3 and R_4 can be either straight or branched-chain alkyl groups, and can be the same or different groups.

When the simple diesters embodying the invention are desired, they are prepared by reacting at an elevated temperature, such as at about 200° C., one molar proportion of a propanediol of the formula:



Compound II

with about two (e.g. 2.1) molar proportions of a monocarboxylic acid containing 5–13 carbon atoms, such acid

being either straight or branched chain. The esters thus obtained are characterized by having a very low pour point, high thermal stability, and good viscosity characteristics over a relatively wide temperature range. When mixed diesters are desired, one molar proportion of Compound II is reacted with a molar proportion of each of two different monocarboxylic straight or branched-chain esters. By the use of different acids in preparing the diesters, the viscosity characteristics can be varied as desired. The diesters embodying the invention can be diesters of any of the 2,2-dialkyl propanediols within the generic formula set out for Compound II. The acids employed are aliphatic acids and preferably fatty acids of the acetic acid series or branched-chain derivatives thereof, although they can be acids which contain an ether linkage in the chain. The propanediol is desirably esterified with pelargonic acid alone or together with another aliphatic monocarboxylic acid, although another particularly useful group of acids for preparing the diesters of the invention are the branched-chain "oxo" acids which are prepared by the reaction of carbon monoxide and hydrogen on the olefins obtainable from petroleum, with oxidation of the resulting aldehydes.

These "oxo" acids have a highly branched structure and are derived from such materials as propylene trimers, propylene tetramers, isobutylene trimers, isobutylene tetramers, the C_7 olefins, and similar well known olefins. If desired, any of the other aliphatic straight or branched-chain monocarboxylic acids containing at least 5 carbon atoms can be used. Thus, for example, suitable acids are the fatty acids such as pelargonic acid, caproic acid, lauric acid, myristic acid, palmitic acid, stearic acid, and the like; simple branched-chain acids such as 2-ethylbutyric acid, 2-ethyl-hexanoic acid, 2-octanoic acid, and the like; and the branched-chain "oxo" acids such as "decylic" acid derived from propylene trimers, "tridecylic" acid derived from propylene tetramer or from isobutylene trimer, the branched-chain acids of the formula

$$C_8H_{17}COOH$$

derived by the oxo reaction from diisobutylene and similar well known branched-chain "oxo" acids, as well as any of the other well known aliphatic acids containing at least 4 carbon atoms.

The diester lubricants embodying this invention can be used alone, particularly in applications where it is undesirable to employ additives which would leave a residue or which might decompose or be volatile at elevated temperatures. In some cases, however, it is desirable to employ propanediol esters as defined herein in conjunction with such additives as antioxidants, anticorrosion agents, pour point depressors, viscosity improvers, or extreme pressure additives. The synthetic lubricants embodying the invention can also be used in the formulation of greases by the usual methods, as well as being used in admixture with hydrocarbon lubricating oil, another synthetic ester lubricant, mineral oil, or any of the other well known lubricating materials.

By varying the nature of the acid used to esterify the diol, a variety of products having a wide range of viscosity and pour point characteristics can be obtained. In most cases, the acid employed will contain at least 7 carbon atoms and desirably from 7 to 12 carbon atoms, although the synthetic fatty acids having chain lengths of as much as 30 carbon atoms or more can be used in some cases, particularly where a low pour point is not necessary.

These lubricants are readily prepared as mentioned above by heating about 2 molar equivalents (preferably about 2.1) of the desired acid or acids as defined herein with 1 molar equivalent of the 2,2-dialkyl-propanediol (Compound II). The conditions under which the esterification is effected can be varied in accordance with well known practice for effecting esterification of an alcohol with an acid. In most cases, it is desirable to heat the mixture of the acid and the substituted propanediol to a temperature of about 150–200° C. for a time sufficient to cause evolution of 2 molar equivalents of water. If desired, this water can be removed as formed, but this is not necessary. When the water is removed, an entraining solvent such as xylene or Stoddard solvent can be used, or the water can be distilled off without the use of a solvent. When esterification is substantially complete, the diesters obtained are preferably washed with an alkaline material to remove unreacted acid and are then preferably distilled at reduced pressure as in a molecular still.

Among the substituted propanediols which are suitable for use in practicing the invention are such materials as 2,2-diethyl-1,3-propanediol, 2-ethyl-2 - n - propyl-1,3-propanediol, 2-ethyl-2-n-butyl-1,3-propanediol, 2-ethyl-2-sec.-butyl-1,3-propanediol, 2-ethyl - 2 - iso-propyl-1,3-propanediol, 2-n-propyl-2-n-butyl-1,3-propanediol, 2-n-propyl-2-isobutyl-1,3-propanediol, 2-n-propyl - 2 - sec.-butyl-1,3-propanediol, 2-isopropyl-2-n-propyl-1,3 - propanediol, 2,2-di-n-propyl-1,3-propanediol, 2,2 - di - isopropyl - 1,3-propanediol, 2,2-di-n-butyl-1,3-propanediol, 2-n-butyl-2-isobutyl-1,3-propanediol, 2 - n - butyl-2-sec.-butyl-1,3-propanediol, 2,2-di-isobutyl - 1,3 - propanediol, 2,2 - di - sec.-butyl-1,3-propanediol, and similar propanediols as defined hereinabove.

The viscosity and pour point characteristics of diesters prepared by reacting various substituted propanediols as defined herein with various acids as defined above are set out in Table I. The viscosity data set out in the various tables was determined by ASTM Method D–88–44, and the pour point data by modification of ASTM Method D–97–47.

Although the propanediol is generally most desirably esterified with pelargonic acid when a simple diester is being employed, any of the other above described aliphatic monocarboxylic acids can be used.

TABLE I

Physical Properties of Esters of 2,2-Dialkyl-1,3-Propanediols

Ester	Pour point, ° F.	Viscosity, centistokes		
		210° F.	100° F.	−65° F.
2,2-diethyl-1,3-propanediol dipelargonate.	Below −60	2.94	11.46	7,593
2-butyl-2-ethyl-1,3-propanediol dipelargonate.	do	3.39	14.63	15,647
2,2-diethyl-1,3-propanediol diundecanoate.	About −60	3.85	16.58	Solid
2-ethyl-2-isobutyl-1,3-propanediol dipelargonate.	Below −65	3.24	13.08	10,041
2,2-di-isobutyl-1,3-propanediol dioctanoate.	do	3.09	12.49	10,108
2-butyl-2-ethyl-1,3-propanediol heptanoate-undecanoate mixed ester.	Below −60	3.85	15.20	Solid
2-ethyl-2-isobutyl-1,3-propanediol dipelargonate.	Below −65	3.24	13.08	10,041
2-ethyl-2-propyl-1,3-propanediol dipelargonate.	Below −60	3.18	12.77	12,362
2,2-diethyl-1,3-propanediol pelargonate-2-ethyl-hexanoate mixed ester.	do	3.7	12.3	
2,2-diethyl-1,3-propanediol dicaprate.	do	4.1	13.2	
2-ethyl-2-n-butyl-1,3-propanediol di-n-decylate.	do	4.6	15.0	
2,2-diethyl-1,3-propanediol di-2-ethyl-hexanoate.	do	2.8	10.5	
2-ethyl-2-butyl-1,3-propanediol di-2-ethyl hexanoate.	do	3.2	11.5	
2,2-diethyl-1,3-propanediol di-"caprate."	do	3.9	13.0	
2-ethyl-2-n-butyl-1,3-propanediol di-"caprate."	do	4.3	14.6	
2,2-diethyl-1,3-propanediol di-"nonanoate."	do	3.0	11.3	
2-ethyl-2-butyl-1,3-propanediol di-"nonanoate."	do	3.3	11.9	
2,2-diethyl-1,3-propanediol di-"tridecylate."	Below −50	4.7	16.2	
2-ethyl-2-n-butyl-1,3-propanediol di-"tridecylate."	Below −40	5.3	17.9	

The "caprate" diester set out in Table I was the ester of the C_{10} acid derived from propylene trimer by oxidation of the corresponding "oxo" aldehyde and is a mixture of branched-chain diesters from the branched chain acids of the formula $C_9H_{19}COOH$. The "non-anoate" esters are those derived from the branched-chain acids of the formula $C_8H_{17}COOH$ derived by means of the oxo reaction from diisobutylene. The "tridecylate" esters are derived from the branched-chain acids of the formula $C_{12}H_{25}COOH$ derived by means of the oxo reaction from propylene tetramer. As can be seen from Table 2, these lubricants also have excellent viscosity and pour point characteristics.

A particularly useful class of synthetic lubricants is prepared by esterifying a Compound II as defined herein with a mixture of two or more acids. The acids employed can be mixtures of straight and branched-chain acids, mixtures of acids having the same number of carbon atoms but differing in structural configuration, or mixtures of acids having differing numbers of carbon atoms in the molecule. Similarly, the lubricants embodying this invention can be mere mechanical mixtures of two or more esters as described herein. In most cases, however, the mixed esters prepared by esterifying 1 molar proportion of the Compound II with 2 molar proportions of a mixture of acids are preferred to the mechanical mixtures.

By the use of mixtures of acids with one or more species of Compound II as herein defined, the pour points and viscosity characteristics of the diesters can be obtained in any desired range. Thus, for example, if Compound II is esterified with a mixture of 3 acids, R_1COOH, R_2COOH and R_5COOH, wherein each of R_1, R_2 and R_5 is an alkyl group of at least 4 carbon atoms, the resulting mixed product will contain a mixture of several different esters.

Since R_3 and R_4 of Compound II can also be varied, as described herein, a large number of synthetic diesters can be readily prepared. If desired, two or more species of Compound II can be esterified simultaneously with one or more acids. It is often desirable to prepare a lubricant with a particular set of values for the pour point and viscosity characteristics. Thus, for example, lubricants for use in aircraft instruments should be light lubricants having viscosities in the range of 4–8 centistokes at 100° F., whereas the medium lubricants having viscosities in the range of 10–15 centistokes at 100° F. are useful in turbojet engines, and the heavy lubricants having viscosities of 15–25 centistokes at 100° F. are useful for high temperature applications.

Typical examples of synthetic diester lubricants prepared by reacting typical species of Compound II with mixtures of acids are set out in Table I above.

The diester lubricants embodying this invention not only possess excellent pour point and viscosity characteristics but also exhibit a high degree of thermal stability and resistance to oxidation, especially at elevated temperatures. Even after refluxing at atmospheric pressure for 24 hours at 335° C., the weight loss from the esters of this invention is usually less than about 1 percent, which indicates an initial low content of volatile material as well as low degree of decomposition. Furthermore, the color of the lubricants is substantially unchanged, and they contain no free acid.

Thus, by means of this invention, a highly useful class of synthetic ester lubricants and functional fluids is provided. Their physical and chemical characteristics make them particularly suitable for use as lubricating oils in applications where hydrocarbon lubricating oils are now used, and particularly in high temperature applications where hydrocarbon lubricating oils and most synthetic esters are unsuitable. For example, in an oxidation test at 500° F. 2-methyl-2-ethyl-1,3-propanediol dipelargonate was oxidized to a nonflowing grease while 2,2-diethyl-1,3-propanediol dipelargonate suffered only a 422 percent change in viscosity and remained a usable lubricating oil when exposed to the same conditions. Further evidence of this unexpected stability will be found in the examples given later. These esters also show good oxidative stability at lower temperatures but the exhibition of unusual or unexpected oxidative stability as compared to other 2,2-dialkyl-1,3-propanediol esters only appears at high temperatures.

From the data it can be seen that this high stability depends on having both of the 2-alkyl groups larger than methyl. We know of no reason based on theoretical grounds why such structures have greatly enhanced stability at high temperatures.

While the data shown in the examples are all derived from lubricating compositions containing specific antioxidants, the stability is an inherent characteristic of the structure of the defined esters of this invention and is not dependent on the use of any specific antioxidant. A number of suitable high temperature antioxidants can be used with these esters to provide stable compositions, however, many are useless. The oxidation of any ester in the absence of an antioxidant is so rapid in these very high temperature tests as to preclude testing the neat esters. The trend in design of jet engines is towards higher and higher bearing temperatures. Previously reasonable stability at 425° F. was considered a sufficient degree of stability for a jet lubricant. However, the test temperatures now proposed are 500°–550° F. Very few esters remain fluid for any appreciable time in the presence of air at 500°, even when protected by an antioxidant. The esters herein disclosed and when protected do remain usable fluids for some hours at this temperature.

In addition to high thermal stability these esters have excellent viscosity properties at both high and low temperatures, low pour points and other physical properties which make them very desirable lubricants and valuable functional fluids for other purposes such as in hydraulic applications.

Although either straight or branched-chain acids can be used in preparing the diesters of the invention, the effect of the branched-chain is particularly noticeable in the viscosity characteristics of the product. Thus, the branched-chain diesters prepared by use of the oxo acids remain fluid at low temperatures for higher molecular weights than is the case with the straight-chain diesters.

The data in Table II below was obtained using the esters of this invention wherein the ester was stabilized with either 1% phenothiazine (P) or 1% phenyl-α-naphthylamine (PANA) plus 1% diphenylamine (DPA). The test was carried out using a 25-ml. sample of the ester, containing a piece of steel 1" x ¼" x 1/32", heated in an electrically heated block at the desired temperature. Air was passed through the sample at the rate of 5 liters/hour. Tests were carried out at 500° F. for 20 hours and at 550° for 9 hours. The 100° F.-viscosity was determined at the end of the test period if possible. Results, reported in Table II below, given as percent increase in viscosity from that of the original unoxidized ester. As can be seen, the diesters of this invention retain their fluid character with viscosity increase after 9 hours at 550° F. of less than about 10 times (1,000%) under the described oxidative test conditions. In contrast, the table shows that homologous diesters under the same test conditions undergo much greater viscosity increases and in some cases become greases or solids even under less rigorous test conditions.

TABLE II

Oxidative Stability of Esters of 2,2-Dialkyl-1,3-Propanediols

Ester	Antioxidant [1]	Viscosity increase after test	
		20 hours at 500° F.	9 hours at 550° F.
2,2-dimethyl-1,3-propanediol dipelargonate.	1% P	726%	Grease.[2]
	1% PANA+1% DPA	Grease [2]	
2-ethyl-2-methyl-1,3-propanediol dipelargonate.	1% P	1475%	1652%.
	1% PANA+1% DPA	Grease	Grease.
2-methyl-2-propyl 1,3-propanediol dipelargonate.	1% P	1394%	Solid.
	1% PANA+1% DPA	Grease	Do.
2,2-diethyl-1,3-propanediol dipelargonate.	1% P	303%	431%.
	1% PANA+1% DPA	422%	565%.
2-n-butyl-2-ethyl-1,3-propanediol dipelargonate.	1% P	579%	
	1% PANA+1% DPA	474%	281%.
2,2-diethyl-1,3-propanediol diundecanoate.	1% P		
	1% PANA+1% DPA	468%	320%.
2,2-di-isobutyl-1,3-propanediol dioctanoate.	1% P	458%	
2-n-butyl-2-ethyl-1,3-propanediol heptanoate-undecanoate.	1% P	564%	609%.
	1% PANA+1% DPA	487%	429%.
2-ethyl-2-n-propyl-1,3-propanediol dipelargonate.	1% P	321%	456%.
	1% PANA+1% DPA	347%	369%.

[1] P=phenothiazine, PANA=phenyl-α-naphthylamine, DPA=diphenylamine.
[2] Grease indicates the material would not flow at 100° F.

In addition to the above data, the following results were obtained as to 2 - ethyl - 2 - isobutyl - 1,3 - propanediol dipelargonate.

Oxidative stability employing 1% PANA+1% N-ethyl-phenothiazine as antioxidants was: 52% viscosity increase after 85 hours, test temperature 425° F.

These data show that this ester also possesses desirable properties analogous to those found for the esters set forth above in Table II.

have been incorporated lies between about 0.1% to 5.0%. The most practicable range would probably be from 0.2% to 2.0% for most currently available antioxidants. Not all antioxidants useful for lube-oils are effective. Rather unobviously it appears that nitrogenous antioxidants are especially preferred. Typical effective nitrogenous antioxidants which can be used include those in the tables of data and include:

N,N'-diphenyl-p-phenylenediamine,
N,N'-di(2-naphthyl)-p-phenylenediamine,
Diphenylamine,
Di-α-naphthylamine,
Di-β-naphthylamine,
N-phenyl-α-naphthylamine,
Phenothiazine,
Acridine,
Carbazole,
Ring-alkylated and nitrogen-alkylated derivatives of the above, etc.

Phenolic antioxidants are not effective; those tested include 2,4,6-trialkylphenols, alkylidene-bisphenols and alkylated bisphenols.

Such antioxidant compounds are members of the group of organic antioxidant compounds having a nitrogen atom within a cyclic ring, compounds having a nitrogen atom attached directly to a cyclic ring and compounds having a hydroxy radical attached to a benzene ring. Such compounds generally have from about 6 to about 30 carbon atoms.

Additional tests were carried out using a 250 ml. sample of oil which is placed in a glass tube containing a 1" x 1" x 1/32" polished steel plate. The oil is heated to 425° F. and air is blown through at the rate of 96 l./hr. At 20-hour intervals the oil is cooled and a 10-ml. sample is removed for determination of viscosity and acid number. Oil evaporation loss is replaced at the end of each 20-hour cycle. The results of this test are given in Table III. These data clearly show the superiority over the esters of a 2-methyl-2-alkyl-1,3-propanediol.

TABLE III

Diester (containing 1% N-ethyl phenothiazine+1% p,p'-dioctyldiphenylamine	Oxidative stability of diesters at 425° F.												
	100° F. viscosity increase (percent) after oxidation for hours given						Acid number after oxidation for hours given						
	20	40	60	80	100	120	0	20	40	60	80	100	120
2,2-dimethyl-1,3-propanediol dipelargonate	23.4	18.2	71.4	267	(1)	(1)	0.2	2.1	1.8	4.7	8.9	------	------
2-ethyl-2-methyl-1,3-propanediol dipelargonate	5.7	10.7	128	219	(1)	(1)	0.2	1.1	1.9	10.9	12.8	------	------
2-butyl-2-ethyl-1,3-propanediol dipelargonate	12.0	16.8	23.6	30.9	39.6	49.7	0.04	1.1	1.9	2.6	3.4	3.5	5.7
2-ethyl-2-isobutyl-1,3-propanediol dipelargonate	9.5	13.4	19.1	25.8	31.2	39.2	0.13	------	1.52	2.64	2.15	3.10	3.10

[1] Too thick to measure viscosity at 100° F.

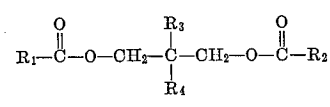
The physical properties of the esters of the present invention in general include a pour point below −50° F., viscosity at 100° F. greater than 11 cs. and viscosity at −65° F. of 30,000 cs. or less. It is not now possible to suggest a specific requirement as to viscosity change in the 500° F. oxidation test. No standard method has been established for this test and the results are greatly influenced by minor changes in test conditions. In addition, it is not now known what increases in viscosity can be tolerated in actual use nor how the tests now being used correlate with in-use high-temperature oxidation. A general statement might be made that the oil must remain a usable fluid after being subjected to the 500° F. oxidation test carried out as described herein.

A useful range of the antioxidants tested so far which

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

We claim:

1. A synthetic functional fluid consisting essentially of at least one diester of the formula:



wherein each of R_1 and R_2 is an alkyl group containing 4–12 carbon atoms and R_3 and R_4 are alkyl groups con-

taining 2–4 carbon atoms, said fluid having a pour point below about −40° F., a viscosity at 100° F. greater than about 10.5 cs. and a viscosity at −65° F. of less than about 30,000 cs.

2. A synthetic functional fluid as defined by claim 1 consisting essentially of a diester of 2,2-diethyl-1,3-propanediol and from one to three different saturated aliphatic monocarboxylic acids containing 5–13 carbon atoms.

3. A synthetic functional fluid as defined by claim 1 consisting esentially of a diester of 2-ethyl-2-n-propyl-1,3-propanediol and from one to three saturated aliphatic monocarboxylic acids containing 5–13 carbon atoms.

4. A synthetic functional fluid as defined by claim 1 consisting essentially of a diester of 2-ethyl-2-n-butyl-1,3-propanediol and from one to three saturated aliphatic monocarboxylic acids containing 5–13 carbon atoms.

5. A synthetic functional fluid as defined by claim 1 consisting esentially of a diester of 2-ethyl-2-isobutyl-1,3-propanediol and from one to three saturated aliphatic monocarboxylic acids containing 5–12 carbon atoms.

6. A synthetic functional fluid as defined by claim 1 consisting essentially of the pelargonate diester of 2,2-diethyl-1,3-propanediol.

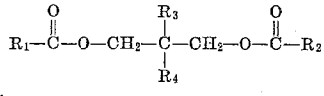
7. A synthetic functional fluid as defined by claim 1 consisting essentially of the pelargonate diester of 2-ethyl-2-n-propyl-1,3-propanediol.

8. A synthetic functional fluid as defined by claim 1 consisting essentially of the pelargonate diester of 2-ethyl 2-n-butyl propanediol-1,3.

9. A synthetic functional fluid as defined by claim 1 consisting essentially of the undecanoate diester of 2,2-diethyl-1,3-propanediol.

10. A synthetic functional fluid as defined by claim 1 consisting essentially of the mixed heptanoate-undecanoate diester of 2-n-butyl-2-ethyl-1,3-propanediol.

11. A synthetic functional fluid consisting essentially of at least one diester of the formula:



wherein each of R_1 and R_2 is an alkyl group containing 4–12 carbon atoms and R_3 and R_4 are alkyl groups containing 2–4 carbon atoms, said fluid having a pour point below about −40° F., a viscosity at 100° F. greater than about 10.5 cs. and a viscosity at −65° F. of less than about 30,000 cs., said fluid containing from about 0.1 to about 5% by weight of an organic nitrogenous antioxidant compound selected from the group consisting of (1) phenothiazine, (2) phenothiazine having a hydrocarbon radical as an N-substituent, (3) secondary diaromatic amines, and mixtures of these nitrogenous antioxidant compounds, whereby the fluid is characterized in that 5 liters/hour of air passed into the fluid at 550° F. for 9 hours produces a viscosity increase of no greater than 10 times.

12. A fluid as defined by claim 11 wherein the diester is the pelargonate diester of 2,2-diethyl-1,3-propanediol.

13. A fluid as defined by claim 11 wherein the diester is the pelargonate diester of 2-ethyl-2-n-propyl-1,3-propanediol.

14. A fluid as defined by claim 11 wherein the diester is the pelargonate diester of 2-ethyl-2-n-butyl propanediol-1,3.

15. A fluid as defined by claim 11 wherein the diester is the undecanoate diester of 2,2-diethyl-1,3-propanediol.

16. A fluid as defined by claim 11 wherein the diester is the mixed heptanoate-undecanoate diester of 2-n-butyl-2-ethyl-1,3-propanediol.

17. A fluid as defined by claim 11 wherein the antioxidant compound is N-ethyl phenothiazine.

18. A fluid as defined by claim 11 wherein the antioxidant compound is diphenylamine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,499,984	Beavers et al.	Mar. 7, 1950
2,798,083	Bell et al.	July 2, 1957
2,971,912	Elliot et al.	Feb. 14, 1961
2,991,252	Pethrick et al.	July 4, 1961

OTHER REFERENCES

(A) Industrial and Engineering Chemistry, vol. 45, No. 8, pages 1766–1775, page 1771 pertinent.

(B) Industrial and Engineering Chemistry, vol. 42, No. 12, pages 2415, 2434 and 2444.

"Synthetic Lubricants," McTurk, October 1953, Wright Air Development Center Technical Report, 53–88; reproduced by Document Service Center, Knott Building, Dayton 2, Ohio, pages 26–28.

UNITED STATES PATENT OFFICE

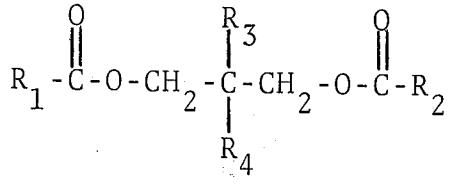
CERTIFICATE OF CORRECTION

Patent No. 3,148,147 September 8, 1964

Alan Bell et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 51 to 54, the formula should appear as shown below instead of as in the patent:



column 11, line 21, for "5-12" read -- 5-13 --.

Signed and sealed this 18th day of May 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents