United States Patent

Malec

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[54] SYNTHETIC LUBRICANTS

[72] Inventor: **Robert E. Malec, Birmingham, Mich.**

[73] Assignee: **Ethyl Corporation, New York, N.Y.**

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[52] **U.S. Cl.** .....**260/410.6, 260/488 J, 252/49.9**

[51] **Int. Cl.** **C07c 69/20, C07c 69/32, C11c 3/08**

[58] **Field of Search**.....260/410.6, 488 J

[56] **References Cited**

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Primary Examiner—Lorraine A. Weinberger
Assistant Examiner—R. S. Weissberg
Attorney—Donald L. Johnson

[57] **ABSTRACT**

Elimination of water from trimethylolpropane forms a mixture containing a substantial amount of di-trimethylolpropane. Esterification of the mixture with monobasic aliphatic carboxylic acids containing from about 2–12 carbon atoms such that the average acid chain is from 4–9 carbon atoms results in a synthetic ester lubricant especially useful for lubricating gas turbines.

9 Claims, No Drawings

SYNTHETIC LUBRICANTS

BACKGROUND

With the development of gas turbine aircraft engines, which must operate at peak efficiency at extremely high altitudes, there has developed needs for lubricants which can endure the extremely high temperatures encountered in these engines for long periods of time and yet remain fluid at the very low temperatures to which these engines are exposed in arctic regions or when the engine is shut down during flight. Engine manufacturers and operations personnel dealing with these engines require a lubricant possessing exceptionally low viscosity at low temperatures and, at the same time, possessing a satisfactory lubricating viscosity at higher temperatures. During the period from about 1940–45,ester lubricants were developed for use primarily in the early turbine engines. The development of these lubricants is described in such publications as Zorn, "Esters as Lubricants," available from the Air Documents Division, T–2 AMC Microfilm No. RC–718 F–18614, Wright Field, Dayton, Ohio, released in July 1947. Following this early work, various modifications of the simple ester lubricants were developed such as the "complex" esters made using both mono- and di-basic acids with mono- and polyhydric alcohols.

SUMMARY

The present invention relates to a new class of esters useful as lubricants for turbine engines under extreme temperature conditions. In particular, this invention relates to monobasic aliphatic carboxylic acid esters of di-trimethylolpropane.

PREFERRED EMBODIMENTS

An object of this invention is to provide ester lubricants which remain liquid at extremely low temperatures and yet maintain a satisfactory lubricating viscosity under operating conditions. These and other objects are accomplished by providing a synthetic ester lubricant made by the process comprising:

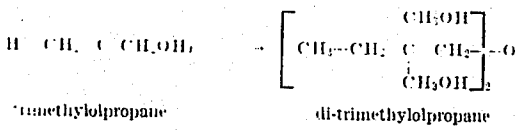
A. heating trimethylolpropane to an etherification temperature in the presence of an acid catalyst causing the elimination of water and the formation of poly-trimethylolpropane,

B. maintaining said trimethylolpropane at said etherification temperature until from about 0.25 to 0.75 mole parts of water have been eliminated for each mole part of said trimethylolpropane,

C. adding sufficient monobasic aliphatic carboxylic acid to the resultant poly-trimethylolpropane to esterify substantially all of the hydroxyl groups present, said monobasic aliphatic carboxylic acid containing from about 2–12 carbon atoms in proportion such that the average acid group contains from about 4–9 carbon atoms, and

D. heating the mixture of said monobasic aliphatic carboxylic acid and poly-trimethylolpropane to an esterification temperature and maintaining said mixture at said esterification temperature until esterification is substantially complete.

The first step in the preparation of the esters is an etherification stage during which trimethylolpropane is heated causing the elimination of water with the formation of an ether linkage according to the following equation.



trimethylolpropane — di-trimethylolpropane

This is an oversimplification of the process because, in practice, some di-trimethylolpropane undergoes further ether formation forming some trimethylolpropane and higher ethers. Accordingly, the polyol from which the final ester is derived in this embodiment is best described by defining the process used.

The trimethylolpropane is first heated to an etherification temperature — that is, a temperature high enough to cause the elimination of water according to the foregoing equation. This can be done at temperatures from about 100–250° C. The elimination of water is facilitated if a small catalytic amount of an acid is added. Good results are obtained with about 1–10 parts of acid catalyst per 100 parts of trimethylolpropane. The preferred acid catalysts are the strong mineral acids such as phosphoric, phosphorous, hydrochloric, sulfuric, p-toluene sulfonic, acid ion exchange resins such as sulfonated polystyrenes cross-linked with divinylbenzene (Dow X–50W) and other similar acidic compounds. The preferred catalysts are the sulfonated organic compounds such as benzene sulfonic acid, toluene sulfonic acid, xylene sulfonic acid, dodecyl benzene sulfonic acid, petroleum sulfonic acids, sulfonated alkanes, and especially the acidic ion exchange resins such as the above sulfonated polystyrene resin. The ion exchange resins are especially preferred because they can be readily removed from the reaction zone by filtration, making it easier to obtain a neutral product.

It is preferred, although not required, to have a water azeotroping solvent in the reaction mixture to aid in the removal of water. These are materials which will co-distill with the water as it forms. When condensed, they separate from the water, allowing the water to be drained off and the solvent to be returned to the reaction zone. This allows the rapid removal of water at much lower temperatures. Useful azeotroping solvents include hydrocarbons and chlorinated hydrocarbons boiling from about 80–175°C. They include heptane, octane, isooctane, n-decane, isodecane, benzene, toluene, xylene, mesitylene, chloroform, carbon tetrachloride, chlorobenzene, and the like. The most preferred azeotroping agents are toluene and xylene.

As stated above, heating the trimethylolpropane at an etherification temperature is continued until about 0.25–0.75 moles of water have been formed per each mole of starting trimethylolpropane. This insures that a substantial amount of ditrimethylolpropane has formed, and at the higher limit, causes the formation of some tri-trimethylolpropane and higher ethers. Esters of polyol mixtures formed within these limits have exceptionally good lubricating properties.

After the desired amount of water has been removed, sufficient monobasic aliphatic carboxylic acid is added to completely esterify the remaining hydroxyl radicals. The required amount is easily calculated from the amount of initial trimethylolpropane and the amount of water that has been removed. The acids used are monobasic aliphatic carboxylic acids containing from about 2–12 carbon atoms. These include acetic, propionic, butyric, isobutyric, valeric, caproic, enanthylic, caprylic, pelargonic, capric, undecylic, and lauric. Although branched chain acids can be used, it is preferred that the acids be substantially straight chain. Sometimes the physical properties of the lubricant can be improved by incorporating a small amount, up to about 25 per cent, of pivalic acid.

The amount of each acid employed should be in proportion such that the average acid group contains from 4–9 carbon atoms; for example, if 50 mole per cent of the acid used is n-butyric acid and 50 mole per cent is n-octanoic acid (caprylic), then the weighted average acid group contains 6 carbon atoms. If only a single acid or a mixture of acids all containing the same number of carbon atoms are used, then the acid must contain from 4–9 carbon atoms in order for the weighted average acid to contain from 4–9 carbon atoms.

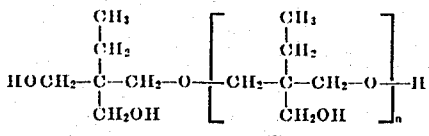
Especially preferred products are obtained by using as the carboxylic acid either n-octanoic acid alone or a mixture consisting essentially of 15–20 weight per cent n-hexanoic acid, 35–40 weight per cent n-octanoic acid and 40–50 weight per cent n-decanoic acid. The use of the foregoing acids gives esters having exceptional viscosity properties.

The esterification is readily carried out by heating the mixture to an esterification temperature of from about 100–250° C. Although a catalyst is not required as shown by U.S. Pat.

No. 2,991,297, this step is aided by the use of an esterification catalyst. Acids are especially useful in this function. A convenient way to conduct this step when an acid has been used in the etherification stage is to merely leave the etherification acid catalyst in the poly-trimethylolpropane mixture and it will function as an esterification catalyst because the same acids are effective in both stages. The same is true of the azeotroping solvent. If one has been used in the etherification stage it can merely be left in the reaction mixture because water is also formed during the esterification stage and this also must be removed. The same azeotroping agents previously mentioned are useful in this function.

The mixture of carboxylic acids and poly-trimethylolpropanes is held at an esterification temperature until the hydroxyl groups are substantially all esterified. This can be determined by merely measuring the water removed or by following the disappearance of hydroxyl radicals by infrared analysis.

When the esterification is complete any solvent present is distilled off. It is sometimes desirable to first wash the ester with water or an aqueous alkaline solution such as sodium carbonate to remove any residual acid that may be present. The ester can be finally dried by distilling out any solvent and residual water up to a temperature of about 200° C. at about 5 mm. The final product consists mainly of a substantially fully esterified monobasic aliphatic carboxylic acid ester of a mixture of polyhydric alcohols, said mixture consisting essentially of alcohols having the formula:



(I)

wherein n is an integer from 0 to about 4 such that the average value of n for said mixture is from about 0.5 to 1.5, said monobasic aliphatic carboxylic acid containing from 2–12 carbon atoms in proportions such that the average acid chain contains from about 4–9 carbon atoms.

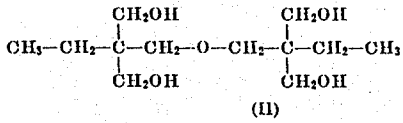
By stating that n has an average value of 0.5 to 1.5 is meant that, although n is an integer from 0–4 in the individual polyols in the polyol mixture from which the ester is made, the mixture contains compounds having different values of n from 0–4, in such proportion that the average value of n is from 0.5 – 1.5. For example, in a mixture consisting only of 50 mole per cent trimethylolpropane (n=0) and 50 mole per cent di-trimethylolpropane (n=1), the average value of n is 0.5.

Preferably the average value of n is from 0.9 – 1.1. These mixtures contain a maximum amount of di-trimethylolpropane and result in superior lubricants.

As in the previous embodiment, the most preferred esters are those made from either n-octanoic acid or a mixture of n-hexanoic acid, n-octanoic acid and n-decanoic acids in proportions such that the average acid chain contains from 8–9 carbon atoms. A preferred acid mixture meeting this requirement is a mixture consisting essentially of 15–20 weight per cent n-hexanoic acid, 35–40 weight per cent n-octanoic acid and 40–50 weight per cent n-decanoic acid.

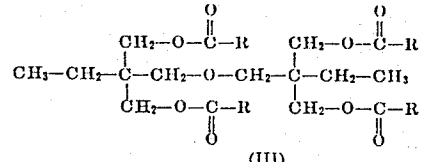
It is apparent from the foregoing that the ester mixtures described contain a substantial amount of a fully esterified mono-basic aliphatic carboxylic acid ester of di-trimethylolpropane in which the acid or acids used to form the ester contain from 2–12 carbon atoms and are present in proportion such that the average acid contains from 4–9 carbon atoms.

Di-trimethylolpropane has the formula:



(II)

and its fully esterified ester has the formula:



(III)

Accordingly, an embodiment of the present invention is the above fully esterified monobasic aliphatic carboxylic acid ester of di-trimethylolpropane in which R represents an aliphatic hydrocarbon radical which together with the carboxylic group contains from 2–12 carbon atoms in proportion such that the average is from 4–9 carbon atoms. Especially preferred embodiments are the tetra-n-octanoic acid ester of di-trimethylolpropane and the fully esterified product obtained by esterifying di-trimethylolpropane with a mixture of acids consisting essentially of from about 15–20 weight per cent n-hexanoic acid, about 35–40 weight per cent n-octanoic acid and about 40–50 weight per cent n-decanoic acid.

The following examples serve to illustrate the ester lubricants of this invention.

EXAMPLE 1

Formation of Di-Trimethylolpropane

Into a reaction vessel fitted with a stirrer, thermometer and Dean-Stark water separator was placed 268 parts of trimethylolpropane, 150 parts of xylene and 2 parts of p-toluene sulfonic acid. The mixture was stirred and heated to a temperature of 200° C., allowing some of the toluene to distill out. It was refluxed at this temperature until 18 parts of water were removed by means of the water separator. The resultant mixture contained a substantial amount of di-trimethylolpropane together with a small amount of unreacted trimethylolpropane and some higher polytrimethylolpropanes.

Esterification

Into a second reaction vessel was placed 62.5 parts of the di-trimethylolpropane prepared above together with 144 parts of n-octanoic acid. Then 155 parts of xylene were added and the mixture refluxed overnight using a Dean-Stark water separator. The amount of water removed indicated complete esterification and the mixture was then washed with aqueous sodium carbonate and then with water until neutral. It was dried over anhydrous calcium sulfate and then the solvent and any volatile material distilled off by heating first to 100° C. at 20 mm. and then to 150° C. at 1 mm. The resultant product was a clear fluid having the following physical properties.

Viscosity at −40°F.	7399 centistokes
Viscosity at 100°F.	26.08 centistokes
Viscosity at 210°F.	5.06 centistokes
Viscosity index	135
Pour point	−75°F.

The above physical properties show that the ester complies with Navy Specification MIL-L-23699A for lubricants used in jet aircraft engines. The physical properties called for by this specification are:

Viscosity at −40°F.	13,000 centistokes maximum
Viscosity at 100°F.	25 centistokes minimum
Viscosity at 210°F.	5.0–5.5 centistokes
Pour point	−65°F. maximum

EXAMPLE 2

In the reaction vessel as described in Example 1, a decanoic acid ester of di-trimethylolpropane is prepared as follows. Into the reaction vessel was placed a mixture of 68 parts of the di-trimethylolpropane product prepared in Example 1, 172 parts of n-decanoic acid, 1 part of p-toluene sulfonic acid and 155 parts of xylene. The mixture was refluxed overnight while

removing the water formed by esterification. The resultant product was diluted with petroleum ether, washed with aqueous sodium carbonate and then with water until neutral. It was dried over anhydrous calcium sulfate and the petroleum ether and xylene distilled off up to a temperature of 150° C. at 5 mm.

EXAMPLE 3

Another synthetic ester lubricant base was made by placing in the reaction vessel described in Example 1 a mixture of 17 parts of n-hexanoic acid, 38 parts of n-octanoic acid, 45 parts of n-decanoic acid, 40 parts of the di-trimethylolpropane prepared in Example 1, 86 parts of xylene and 1 part of p-toluene sulfonic acid. This mixture was refluxed overnight while removing water with the Dean-Stark water separator. Substantially complete esterification was obtained as shown by the amount of water removed. The ester was then diluted with petroleum ether, washed with aqueous sodium carbonate, and then with water until neutral. It was then dried over anhydrous calcium sulfate and filtered. The petroleum ether, xylene and other volatiles were removed by distillation under vacuum up to a liquid temperature of 150° C. at 5 mm. The resultant mixed ester had the following physical properties:

Viscosity at −40°F.	8349 centistokes
Viscosity at 100°F.	27.86 centistokes
Viscosity at 210°F.	5.34 centistokes
Viscosity index	140
Pour point	−70°F.

These properties satisfy the Navy Specification for MIL–L–2 3699A for Series II jet engine lubricants.

EXAMPLE 4

In the reaction vessel of Example 1 was placed a mixture of 15 parts of n-butyric acid, 10 parts of n-hexanoic acid, 20 parts of n-octanoic acid, 55 parts of n-decanoic acid, 44 parts of di-trimethylolpropane (from Example 1), 86 parts of xylene and 1 part of p-toluene sulfonic acid. The mixture was refluxed overnight with water removal and then diluted with petroleum ether and washed with aqueous sodium carbonate and water until neutral. It was dried over anhydrous calcium sulfate and filtered, following which the solvents were distilled out to a liquid temperature of 150° C. at about 1 mm. The product was a synthetic ester lubricant having excellent physical properties.

EXAMPLE 5

To the reaction vessel of Example 1 was added 15 parts of n-hexanoic acid, 20 parts of n-octanoic acid, 50 parts of n-decanoic acid, 15 parts of pivalic acid, 86 parts of xylene, 43.7 parts of di-trimethylolpropane and 1 part of p-toluene sulfonic acid. The mixture was refluxed until about 12 parts of water were collected in the Dean-Stark separator. The product was then diluted with petroleum ether, neutralized and dried as in the previous examples, giving a useful base for a jet engine lubricant.

EXAMPLE 6

To the reaction vessel of Example 1 is added 290 parts of di-trimethylolpropane, 300 parts of xylene, 1 part of sulfonated poly-styrene ion exchange resin, 620 parts of a mixture of 17 weight per cent n-hexanoic acid, 38 weight per cent n-octanoic acid and 45 weight per cent n-decanoic acid. The reaction mixture was refluxed for 8 hours and then filtered. The filtrate was washed with aqueous sodium carbonate and water until neutral. Residual water and solvents are distilled from the resultant tetra-ester di-trimethylolpropane up to a liquid temperature of 150° F. at 1 mm. The product is a base for an ester lubricant having good physical and lubricating properties.

EXAMPLE 7

Following the procedure of Example 6, an ester lubricant is prepared by refluxing 290 parts of di-trimethylolpropane and 620 parts of a mixture of 7 weight per cent acetic acid, 10 weight per cent n-butyric acid, 25 weight per cent n-hexanoic acid, 30 weight per cent primary octanoic acid (10 per cent branched chain), 25 weight per cent primary decanoic acid (90 per cent n-decanoic) and 9 per cent n-dodecanoic acid. The resultant ester contains acyl radicals containing from 2–12 carbon atoms in proportion such that the average of such radicals contains about 8 carbon atoms.

EXAMPLE 8

To a reaction vessel as described in Example 1 is added 300 parts of xylene, 5 parts of sulfonated poly-styrene ion exchange resin, 286 parts of a mixture of 4.7 weight per cent tri-methylolpropane, 81.1 weight per cent di-trimethylolpropane and 14.2 weight per cent tri-trimethylolpropane. There is then added 620 parts of a mixture of 17 weight per cent n-hexanoic acid, 38 weight per cent n-octanoic acid and 45 weight per cent n-decanoic acid. The mixture is refluxed 4 hours while removing water and then filtered. The filtered product is washed with aqueous sodium carbonate and water until neutral. Residual water and solvent are removed by distilling up to 150° C. at 1 mm. The product is a useful base for preparing an ester lubricant formulation.

In the above example, the average molecular weight of the mixture of polyols employed corresponds to the molecular weight of di-trimethylolpropane. In terms of Formula I, n has an average value of 1. As previously described, the mixture may be varied so that the average molecular weight of the polyol mixture gives an average n value of from 0.5 to 1.5. However, in the preferred lubricants n has an average value of from 0.9 to 1.1.

The ester lubricants of this invention are generally employed in a formulation which contains various additives to improve their usefulness. These include wear inhibitors, such as the phosphate esters, for example, tricresyl phosphate, antioxidants including both the aromatic amine type such as N-phenyl-α-napthyl amine, N-phenyl-β-naphthyl amine, and p,p'-dioctyl diphenylamine, and phenolic type such as 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-thiobis(2,6-di-tert-butylphenol), 4,4'-thiobos(6-tert-butyl-m-cresol), and 2,2'-methylenebis(4-chloro-6-tert-butylphenol. The following example represents the preparation of a typical formulation useful for lubricating the bearing surfaces of an aircraft jet engine.

EXAMPLE 9

Into a blending vessel is placed 9500 parts of the ester lubricant according to Example 1, 350 parts of tricresyl phosphate, 75 parts of p,p'-dioctyl diphenylamine and 75 parts of N-phenyl-α-napthyl amine. The mixture is stirred until fully blended. The resultant formulated ester blend is ideally suited as a lubricant for gas turbine engines.

I claim:

1. A synthetic ester lubricant made by the process comprising:

A. heating trimethylolpropane to an etherification temperature in the presence of an acid catalyst causing the elimination of water and the formation of poly-trimethylolpropane,

B. maintaining said trimethylolpropane at said etherification temperature until from about 0.25 to 0.75 mole parts of water have been eliminated for each mole part of said trimethylolpropane,

C. adding sufficient monobasic saturated aliphatic carboxylic acid to the resultant poly-trimethylolpropane to esterify substantially all of the hydroxyl groups present, said monobasic saturated aliphatic carboxylic acid containing from about 2–12 carbon atoms in proportion such that

the average acid group contains from about 4–9 carbon atoms, and

D. heating the mixture of said monobasic saturated aliphatic carboxylic acid and poly-trimethylolpropane to an esterification temperature and maintaining said mixture at said esterification temperature until esterification is substantially complete.

2. The lubricant of Claim 1 wherein said trimethylolpropane is maintained at said etherification temperature until about 0.45 to 0.55 mole parts of water have been eliminated for each mole part of said trimethylolpropane.

3. The lubricant made by the process of claim 2 wherein the etherification steps (A) and (B) are conducted in the presence of a water azeotroping solvent.

4. The lubricant made by the process of claim 3 wherein said monobasic saturated aliphatic carboxylic acid consists essentially of n-octanoic acid.

5. The lubricant made by the process of claim 3 wherein said monobasic saturated aliphatic carboxylic acid is a mixture consisting essentially of from about 15–20 weight per cent n-hexanoic acid, from about 35–40 weight per cent n-octanoic acid, and from about 40–50 weight per cent n-decanoic acid.

6. A process of preparing a synthetic ester lubricant, said process comprising:

A. heating trimethylolpropane to an etherification temperature in the presence of an acid catalyst causing the elimination of water and the formation of poly-trimethylolpropane,

B. maintaining said trimethylolpropane at said etherification temperature until from about 0.25 to 0.75 mole parts of water have been eliminated for each mole part of said tri-methylolpropane,

C. adding sufficient monobasic saturated aliphatic carboxylic acid to the resultant poly-trimethylolpropane to esterify substantially all of the hydroxyl groups present, said monobasic saturated aliphatic carboxylic acid containing from about 2–12 carbon atoms in proportion such that the average acid group contains from about 4–9 carbon atoms, and

D. heating the mixture of said monobasic saturated aliphatic carboxylic acid and poly-trimethylolpropane to an esterification temperature and maintaining said mixture at said esterification temperature until esterification is substantially complete.

7. The process of claim 6 wherein said trimethylolpropane is maintained at said etherification temperature until about 0.45–0.55 mole parts of water have been eliminated for each mole part of said trimethylolpropane.

8. The process of claim 7 wherein said etherification steps (A) and (B) are conducted in the presence of a water azeotroping solvent.

9. The process of claim 8 wherein said monobasic saturated aliphatic carboxylic acid is a mixture consisting essentially of from about 15–20 weight per cent n-hexanoic acid, from about 35–40 weight per cent n-octanoic acid and from about 40-50 weight per cent n-decanoic acid.

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