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# 1-TETRAHYDROFURYL-3,6,9-NONANETRIOL TRIALKANOATES

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Serial No. 674,259

5 Claims. (Cl. 260—347.4)

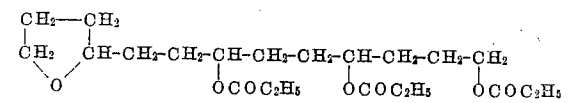
(Granted under Title 35, U. S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a continuation-in-part of application filed October 14, 1953, Serial No. 386,139, now abandoned.

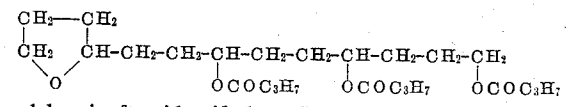
This invention relates to certain esters which find use as extreme low temperature lubricants, namely:

1-tetrahydrofuryl-3,6,9-nonanetriol tripropionate having the formula



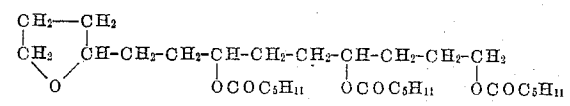
and hereinafter identified as Compound 1;

1-tetrahydrofuryl-3,6,9-nonanetriol tributyrate having the formula



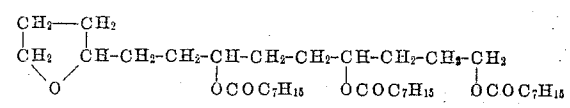
and hereinafter identified as Compound 2;

1-tetrahydrofuryl-3,6,9-nonanetriol tricaproate having the formula



and hereinafter identified as Compound 3;

And 1-tetrahydrofuryl-3,6,9-nonanetriol tricaprylate having the formula



and hereinafter identified at Compound 4.

These esters are liquid and remain so even at exceedingly low temperatures (that is, have low pour points), are essentially non-volatile so that there is no evaporation of the liquids from lubricated bearings even when these are subjected to elevated temperatures, they are stable compounds and hence do not decompose when subjected to elevated temperatures as in overheated bearings or the like, and they exhibit superior lubricating activity over a wide temperature range as shown by their ASTM viscosity slopes and kinematic viscosity indexes. These properties make them admirably suitable as low temperature lubricants, e. g., in internal combustion engines. They also find utility as plasticizers in polyvinyl resins.

Data illustrating these properties is given in the following tables wherein Table I lists the boiling and pour points and Table II lists the viscosity-temperature characteristics of the esters.



*Table I*

BOILING POINTS AND POUR POINTS OF THE ESTERS

| Ester | Boiling point | | Pour point or melting point, ° F. |
|---|---|---|---|
| | Temp., ° C. | Pressure, μHg | |
| Compound 1 | 175 | 40.0 | −41.8 |
| Compound 2 | 150 | 4.0 | −61.1 |
| Compound 3 | 180 | 5.0 | −65.2 |
| Compound 4 | 200 | 2.0 | −58.0 |

*Table II*

VISCOSITY TEMPERATURE CHARACTERISTICS OF ESTERS

| Ester | Viscosity (cs.) | | A. S. T. M. slope | Kinematic viscosity index |
|---|---|---|---|---|
| | 210° F. | 100° F. | | |
| Compound 1 | 4.66 | 31.45 | 0.793 | 50.3 |
| Compound 2 | 4.71 | 26.60 | 0.743 | 104.7 |
| Compound 3 | 5.54 | 31.79 | 0.720 | 122.5 |
| Compound 4 | 6.85 | 40.91 | 0.676 | 131.0 |

A number of the esters were evaluated as plasticizers in polyvinyl resins and found to be generally equal to dioctyl phthalate, and were definitely superior at low temperatures (−70° F.). For example, they may be incorporated in amounts up to 40 percent or higher in Vinylite VYHH (a typical lacquer-type polyvinyl chloride-acetate resin) and Geon 121 (a typical polyvinyl chloride resin used in plastisol formulations). The former gave films equal in strength to dioctyl phthalate plasticized films, and some were superior in compatibility while others were only slightly inferior. In the Geon 121 formulations, all the novel plasticizers tested gave softer specimens than did dioctylphthalate, and all passed the −70° F. brittleness test (loop method) whereas a specimen formulated with dioctylphthalate failed.

The esters of the invention may be prepared by esterifying the required triol with the appropriate acylating agent. The process which we have employed, in most cases, has been to heat the reactants, dissolved in an inert non-aqueous solvent such as benzene, in the presence of a catalytic amount of an acidic catalyst such as p-toluenesulfonic acid. The course of esterification may be followed by separating the water of reaction in such a manner as to enable observation of its rate and quantity.

The trihydroxyalkanes used as starting materials in this invention, and methods for their preparation, are disclosed in a paper by C. R. Russell, K. Alexander, W. O. Erickson, L. S. Hafner, and L. E. Schniepp published in Jour. Am. Chem. Soc. 74, 4543 (1952).

## EXPERIMENTAL

Table III, below, shows the characteristic physical properties of the triesters of this invention, and the methods by which they may be made. It is to be understood, however, that other methods of carrying out the esterification may be employed, as for example by ester interchange as disclosed in U. S. Patent No. 2,476,052.

*Preparation of esters—General procedure.*—From 0.3 to 0.5 mole of the respective triols and an excess of the acids indicated in the table were dissolved in 200 ml. of benzene and 2 g. of p-toluenesulfonic acid added. The reaction mixture was heated to reflux and the course of the reaction followed by the rate of water collection in a separating device attached between the flask and the reflux condenser. When water collection ceased the reaction mixture was cooled and 400 ml. more solvent was added. The solution was extracted with cold aqueous 5 percent sodium hydroxide in an amount slightly

less than that calculated as necessary to neutralize the catalyst and excess acid. The remaining acid was removed by extraction with 10 percent sodium bicarbonate solution. The benzene layer was washed to neutrality with distilled water and then dried over anhydrous magnesium sulfate.

With the products from the higher molecular weight fatty acids it was necessary to add some n-butanol to break up emulsions and facilitate removal of the soaps which formed during these extraction operations.

The dry benzene solutions were filtered and the solvent removed by distillation on a steam-bath. Last traces of solvent and low boiling impurities were removed by heating on a steam-bath under reduced pressure. The crude esters were purified by the methods indicated in Table III. The yields shown in Table III for the once distilled esters are probably 10+% low because of the large holdup in the falling-film type molecular still.

*Purification methods.*—The once distilled esters were reprocessed as necessary to bring their physical properties to a state of constancy and the analytical data into accord with calculated values. These purification steps and the order in which they were applied are indicated in Table III.

*Distillation.*—Two types of apparatus were used for the purification of these products by distillation. Most of the esters were distilled at least once in a falling-film type molecular still equipped with a magnetically operated pumping device for recycling undistilled material. This still was also fitted with a fraction cutter which permitted the collection of three fractions without interrupting the course of the distillation. The still unit was attached to a manifold which was connected to a mercury vapor pump backed by an efficient mechanical pump. All samples were degassed at 125° at 10 to 50 $\mu$ for 1 hour before transferring them to the still.

The second type of apparatus was an alembic flask still similar in design to the still described by J. C. Cowan, L. B. Falkenburg, and H. M. Teeter, Ind. Eng. Chem., Anal. Ed., 16 50 (1944). This still was operated with the boiler completely immersed in an electrically heated oil-bath. A very fine capillary extending to the bottom of the boiler prevented bumping. The use of a fraction cutter permitted the collection of up to five fractions without interrupting the distillation. In addition to its use for complete distillation of some esters, this still was also used for stripping out traces of acids and other low boiling impurities prior to distillation in the falling-film molecular still. This was done by heating the material in the still under high vacuum to a temperature just below the boiling point or, for the higher boiling esters, to a bath temperature of 200°. These conditions were maintained until no more volatile materials were collected.

*Extraction.*—In several cases the complete removal of mono- and di-esters could not be accomplished by distillation alone. These impure esters were dissolved in heptane and the heptane solutions extracted several times with various concentrations of aqueous ethanol. Such extractions are indicated in Table III.

*Table III*

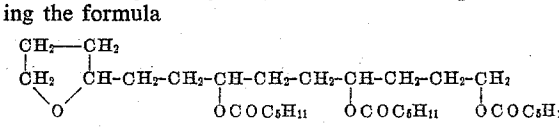
| Ester | Triol, moles | Acid, moles | Time, hrs. | Yield,[a] percent | Purification method | Properties of purified esters: Distillation: Temp., °C.[b] | Distillation: Pressure $\mu$Hg.[c] | $n_D^{25°}$ | $d_4^{20°}$ [d] |
|---|---|---|---|---|---|---|---|---|---|
| Compound 1 | 0.4 | 1.50 | 8.0 | 63 | f,e | 175 | 40.0 | 1.4566 | 1.040 |
| Compound 2 | 0.4 | 1.50 | 8.0 | 66 | i,f | 150 | 4.0 | 1.4558 | 1.008 |
| Compound 3 | 0.3 | 1.05 | 13.0 | 56 | h,f | 180 | 5.0 | 1.4573 | 0.983 |
| Compound 4 | 0.3 | 1.05 | 14.0 | 54 | h, f, i, f | 200 | 2.0 | 1.4596 | 0.954 |

| Ester | Properties of purified esters—Continued: $MD^{20°}$ [b] Calcd. | $MD^{20°}$ [b] Found | Saponification equiv. Calcd. | Saponification equiv. Found | Free acid, percent | Empirical formula | Analyses: Carbon Calcd., percent | Carbon Found, percent | Hydrogen Calcd., percent | Hydrogen Found, percent |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound 1 | 108.27 | 108.74 | 138.2 | 139.0 | 0.59 | $C_{22}H_{38}O_7$ | 63.74 | 63.5 | 9.24 | 9.45 |
| Compound 2 | 122.13 | 123.65 | 152.2 | 153.8 | 0.07 | $C_{25}H_{44}O_7$ | 65.75 | 65.9 | 9.71 | 9.81 |
| Compound 3 | 149.85 | 150.16 | 180.3 | 182.3 | 0.59 | $C_{31}H_{56}O_7$ | 68.83 | 68.5 | 10.43 | 10.28 |
| Compound 4 | 177.57 | 179.44 | 208.3 | 211.0 | 0.20 | $C_{37}H_{68}O_7$ | 71.10 | 71.2 | 10.96 | 10.96 |

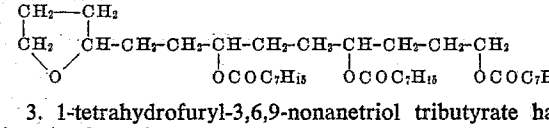
[a] Calculated on the basis of the once distilled product having an analytical purity of 95+ %. All distillations except (e) were carried out on the falling-film still.
[b] Observed on final distillation; temperature of the hot finger of the falling-film still; vapor temperature in alembic flask still.
[c] Measured by McLeod and calibrated thermocouple gauges attached between still and solid $CO_2$ cooled trap.
[d] Measured by Fischer-Davidson gravitometer.
[e] Calculated from $n$ and $d$ values determined at 20°.
[f] Distilled in falling-film molecular still.
[g] Distilled in alembic flask still.
[h] Stripped of low boiling impurities in alembic flask still.
[i] Heptane solution extracted with 60% aqueous ethenol.
[j] Heptane solution extracted with 85% aqueous ethanol.

We claim:

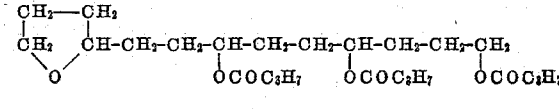
1. 1-tetrahydrofuryl-3,6,9-nonanetriol tricaproate having the formula



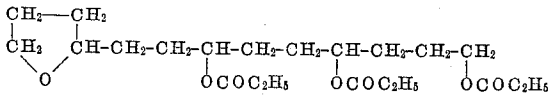
2. 1-tetrahydrofuryl-3,6,9-nonanetriol tricaprylate having the formula



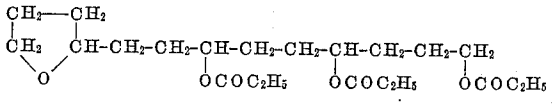
3. 1-tetrahydrofuryl-3,6,9-nonanetriol tributyrate having the formula



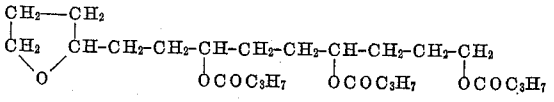
4. 1 - tetrahydrofuryl - 3,6,9 - nonanetriol tripropionate having the formula



5. A compound selected from the group consisting of 1-tetrahydrofuryl-3,6,9-nonanetriol tripropionate having the formula

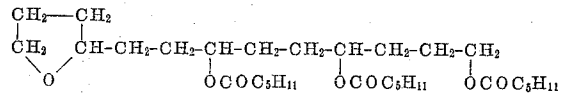


1-tetrahydrofuryl-3,6,9-nonanetriol tributyrate having the formula



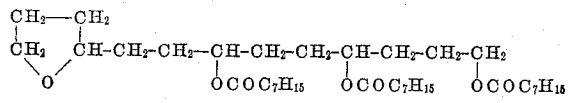


1-tetrahydrofuryl-3,6,9-nonanetriol tricaproate having the formula



and

1-tetrahydrofuryl-3,6,9-nonanetriol tricaprylate having the formula



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