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DI - NEOALKYL $\beta,\beta,\beta^1,\beta^1$ - TETRALOWERALKYL-SUBSTITUTED ALKYLENE DICARBOXYLATES

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2 Claims. (Cl. 260—485)

This application is a division of application Serial No. 210,198, filed July 16, 1962, which was a continuation-in-part of application Serial No. 747,587, filed July 10, 1958, and now abandoned.

This invention relates to ester-type materials which are suitable for use as synthetic lubricants. More particularly, the invention relates to ester-type materials which are derived from acids in which the carbon atom alpha or beta to the carboxyl group is completely substituted with acyclic alkyl groups. Preferably, the substituted carbon atom is the alpha carbon atom.

Military use of turbojet and turboprop aircraft engines has led to a need for specialized engine lubricants. These lubricants must permit starting at very low temperatures encountered in arctic bases. They also must have adequate lubricity and stability at very elevated temperatures. Modern engines have exceedingly high power for their size and put a severe heat stress on the lubricant.

The mineral lubricating oils which possess satisfactory low temperature viscosities have generally been found to have flash points that are dangerously low and high temperature viscosities that are below those required. In other words, when the mineral oil is thin enough at low temperatures, it is too thin and too volatile at higher temperatures. In addition, conventionally refined mineral oils deteriorate too rapidly at high operating temperatures, even when compounded with the best available antioxidants.

Recently, in an effort to obtain the superior lubricants needed for these turbine-type engines, synthetic lubricants have been developed. Esters represent a class of materials which have attracted unusual interest as synthetic lubricants. Diesters are a preferred class of esters. These materials are generally characterized by high viscosity indexes and flash points and lower pour points than mineral oils of a corresponding viscosity.

While the diesters offer many outstanding properties which enable them to be used as lubricants for turbojet and turboprop engines, there remain characteristics in which they may be improved. Two such characteristics are thermal stability and hydrolytic stability.

In the more recent turbines, the normal bearing temperatures during operation reach as high as 475° F. With bearings next to the turbine wheel, a soak-back effect occurs following shutdown. Heat accumulated in the turbine wheel disk flows into the cooler turbine bearings when the oil flow is stopped at time of shutdown. This may add another 100 to 150° F. for a brief period following shutdown. The resulting temperatures are higher than can be withstood by conventional diesters, regardless of compounding with additives. Lack of thermal stability in these materials results in (a) engine deposits and (b) physical loss of lubricant due to partial volatilization of decomposition products.

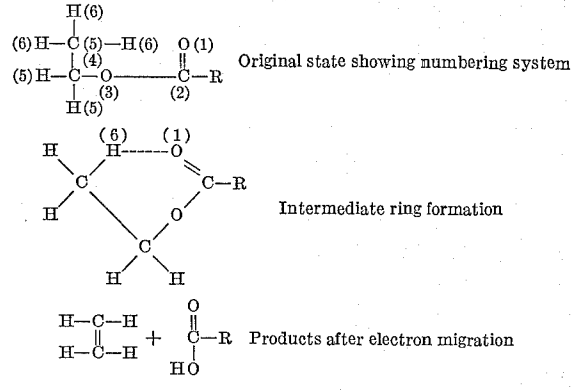
Since all oil systems in aircraft collect small amounts of water from time to time, a diester lubricant should have hydrolytic stability. Lack of hydrolytic stability results in formation of volatile alcohols and corrosive

acids. Currently availaible diesters are not adequately stable.

Broadly stated, the present invention relates to ester-type materials which are derived from organic carboxylic acids in which the carbon atom alpha or beta to the carboxyl group is completely substituted with acyclic alkyl groups. In one embodiment the invention relates to diesters which are derived from dicarboxylic acids in which the carbon atoms alpha to each of the carboxyl groups is completely substituted with acyclic alkyl groups, and from either conventional monohydroxy alcohols or from monohydroxy alcohols in which the beta carbon atom thereof is completely substituted with alkyl groups or fluorine atoms. In a further embodiment the invention relates to diesters which are derived from dicarboxylic acids in which the carbon atoms beta to each of the carboxyl groups is completely substituted with acyclic alkyl groups and from monohydroxy alcohols in which the beta carbon atom thereof is completely substituted with either acyclic alkyl groups or fluorine atoms. In another embodiment the invention relates to esters prepared from monobasic acids in which the carbon atom adjacent to the carboxyl group is completely substituted with acyclic alkyl groups and polyhydroxy alcohols in which the beta carbon thereof is completely substituted with acyclic alkyl groups. In still another embodiment the invention relates to the novel dicarboxylic acids in which the carbon atoms alpha or beta to each of the carboxyl groups is completely substituted with acyclic alkyl groups. In yet another embodiment the invention relates to a process for preparing the afore-mentioned dicarboxylic acids. In yet still another embodiment the invention relates to complex esters which are prepared from (a) the afore-mentioned dicarboxylic acids, (b) the afore-mentioned monobasic acids, (c) the afore-mentioned polyhydroxy alcohols and (d) the afore-mentioned monohydroxy alcohols.

Before proceeding to a description of the suitable starting materials for these ester-type materials, it may be well to set forth an explanation of the heory associated with the function of these materials. While we do not wish to be bound by this explanation, we believe the theory is as follows:

Thermal degradation of esters formed from aliphatic alcohols and aliphatic acids is initiated at the carbonyl oxygen and results in the formation of olefin and acid. This degradation arises from electron migration after formation of an unstable ring structure. To form this intermediate ring there must be hydrogen atoms in the alcohol portion of the ester which are in the sixth atom position from the carbonyl oxygen. These hydrogen atoms must also be coplanar to the carbonyl group or must have rotational freedom if ring formation is to occur. The action is indicated by the following diagram:



Esters in which the "six positions" of the alcohol portion are completely substituted with alkyl groups pre-

vent thermal elimination through this mechanism because the formation of the above foregoing ring structure is not possible and no hydrogens are available in the "six position" for transfer.

Alkyl groups on the alpha carbon of the acid portion of an ester molecule sterically hinder and reduce the availability of the carbonyl oxygen for attack by oxygen, hydrogen, acids, or bases. In other words, the presence of such alkyl groups improves the hydrolytic stability of the ester molecule. The greater the size of the alkyl substituent, the greater would be the hindrance and, accordingly, resistance to hydrolysis. Methyl groups in the alpha position to the carbonyl carbon meet the minimum requirements.

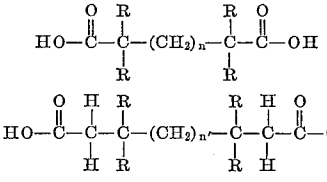
Alcohols with alkyl groups or fluorine atoms on the carbon atom beta to the hydroxyl group, and acids in which the carbon atoms either alpha or beta to the carboxyl groups are completely substituted with alkyl groups, are referred to as "hindered" alcohols and acids. Esters prepared from alcohols and acids, both of which are hindered, possess both thermal and hydrolytic stability. If only the alcohol is hindered, the ester possesses only thermal stability. If only the acid is hindered, the ester possesses only hydrolytic stability.

We have found that substitution only on the beta carbon atoms of the dicarboxylic acid does not produce a noticeable or measurable effect on hydrolytic stability. Still further, we have found that esters prepared from "hindered" alcohol and dicarboxylic acids in which the carbon atoms, either alpha or beta to the carboxyl groups, are completely substituted with alkyl groups exhibit thermal stability greater than is shown when only the alcohol is hindered. This discovery is surprising.

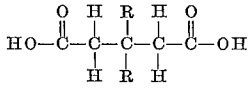
Before giving specific examples of the products and processes of the present invention it may be well at this time to describe the nature of the materials used and the processes involved.

In order to set forth clearly the nature of the present invention the term "ester" as used herein and in the claims refers to the product derived by reacting an organic carboxylic acid with an organic hydroxy compound.

The hindered dibasic acids of the present invention have one of the following formulas:



or



wherein R is an acyclic alkyl group containing from 1 to 4 carbon atoms, n is an integer varying from 1 to 10, and n' is an integer varying from 1 to 9.

Examples of suitable dibasic acids in which the carbon atom alpha to the carboxyl group is completely substituted with acyclic alkyl groups are the following:

Glutaric acids:
- 2,2,4,4-tetraethyl* **
- 2,4-dimethyl-2,4-diethyl*
- 2,4-dimethyl-2,4-dipropyl*
- 2,4-diethyl-2,4-dipropyl
- 2,4-diethyl-2,4-dibutyl* **
- 2,2,4,4-tetramethyl*
- 2,2,4,4-tetrapropyl
- 2,2,4,4-tetrabutyl

Adipic acids:
- 2,2,5,5-tetraethyl* **
- 2,5-dimethyl-2,5-diethyl*

- 2,5-dimethyl-2,5-dipropyl*
- 2,5-diethyl-2,5-dipropyl
- 2,5-diethyl-2,5-dibutyl* **
- 2,2,5,5-tetramethyl*
- 2,2,5,5-tetrapropyl
- 2,2,5,5-tetrabutyl

Pimelic acids:
- 2,2,6,6-tetraethyl* **
- 2,6-dimethyl-2,6-dipropyl*
- 2,6-dimethyl-2,6-diethyl*
- 2,6-diethyl-2,6-dipropyl
- 2,6-diethyl-2,6-dibutyl* **
- 2,2,6,6-tetramethyl*
- 2,2,6,6-tetrapropyl
- 2,2,6,6-tetrabutyl

Suberic acids:
- 2,2,7,7-tetraethyl* **
- 2,7-dimethyl-2,7-diethyl*
- 2,7-dimethyl-2,7-dipropyl*
- 2,7-diethyl-2,7-dipropyl
- 2,7-diethyl-2,7-dibutyl* **
- 2,2,7,7-tetramethyl*
- 2,2,7,7-tetrapropyl
- 2,2,7,7-tetrabutyl

Azelaic acids:
- 2,2,8,8-tetraethyl* **
- 2,8-dimethyl-2,8-diethyl*
- 2,8-dimethyl-2,8-dipropyl*
- 2,8-diethyl-2,8-dipropyl
- 2,8-diethyl-2,8-dibutyl* **
- 2,2,8,8-tetramethyl
- 2,2,8,8-tetrapropyl
- 2,2,8,8-tetrabutyl
- 2,2,8,8-tetraisopropyl
- 2,2,8,8-tetratertiarybutyl

Sebacic acids:
- 2,2,9,9-tetraethyl* **
- 2,9-dimethyl-2,9-diethyl*
- 2,9-dimethyl-2,9-dipropyl*
- 2,9-diethyl-2,9-dipropyl
- 2,9-diethyl-2,9-dibutyl* **
- 2,2,9,9-tetramethyl*
- 2,2,9,9-tetrapropyl
- 2,2,9,9-tetrabutyl

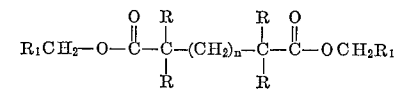
Examples of suitable dibasic acids in which the carbon atom beta to the carboxyl group is completely substituted with acyclic alkyl groups are the following:

Beta acids:
- 3,3-dimethyl glutaric acid*
- 3,3,5,5-tetramethyl pimelic acid
- 3,3,6,6-tetramethyl suberic acid*
- 3,3,6,6-tetraethyl suberic acid*
- 3,6-dimethyl-3,6-diethyl suberic acid*
- 3,3,7,7-tetramethyl azelaic acid
- 3,3,8,8-tetramethyl sebacic acid

Of the suitable acids listed above, the ones indicated with an asterisk are preferred. Of the preferred acids, the ones indicated with a double asterisk are more preferred.

Diesters having improved hydrolytic stability are exceedingly difficult to prepare directly from hindered acids because the hindrance impedes reaction with the alcohol. We have prepared these diesters from the acid chloride of the hindered acid and the sodium salt of the alcohol used.

Diesters prepared from hindered alpha-substituted dibasic acids and conventional alcohols have the following formula:



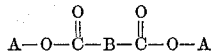
wherein R is an acyclic alkyl group containing from 1 to 4 carbon atoms, R_1 is an acyclic alkyl group containing

from 1 to 10 carbon atoms and *n* is an integer varying from 1 to 10. Examples of suitable conventional alcohols are the following:

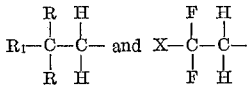
n-Butanol	n-Dodecanol
n-Hexanol*	n-Tridecanol
n-Octanol*	n-Hexadecanol
n-Decanol*	n-Octadecanol
2-ethylhexanol*	2-ethyl butanol
Isooctanol*	Isodecanol

Of the suitable alcohols listed above, the ones indicated with an asterisk are preferred.

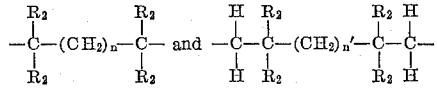
Diesters prepared from hindered dibasic acids and hindered alcohols have the following formula:



where A is selected from

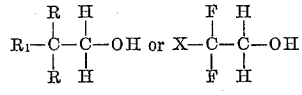


wherein R is an acyclic alkyl group containing from 1 to 4 carbon atoms, R_1 is an acyclic alkyl group containing from 2 to 10 carbon atoms, X is either fluorine or an acyclic fluoroalkyl group containing from 1 to 10 carbon atoms, where B is selected from:



wherein R_2 is an acyclic alkyl group containing from 1 to 4 carbon atoms, *n* is an integer varying from 1 to 10, and *n'* is an integer varying from 1 to 9.

The hindered alcohols of the present invention have one of the following formulas:



where R is an acyclic alkyl group containing from 1 to 4 carbon atoms, R_1 is an acyclic alkyl group containing from 2 to 10 carbon atoms, and X is either fluorine or an acyclic fluoroalkyl group containing from 1 to 10 carbon atoms.

Examples of suitable hindered alcohols are the following:

2,2-dimethyl-1-pentanol*
2,2-diethyl-1-butanol*
2,2-dimethyl-1-hexanol*
2,2-dimethyl-1-butanol
2-methyl-2-ethyl-1-octanol
2,2,4-trimethyl-1-pentanol
2,2-dimethyl-1-octanol*
2,2-dimethyl-1-decanol*
2-methyl-2-propyl-1-pentanol
2-ethyl-2-propyl-1-hexanol
2-methyl-2-tertiary amyl-1-butanol
2-methyl-2-isopropyl-1-hexanol
1H,1H,7H-dodecafluoro-1-heptanol
1H,1H,9H-hexadecanefluoro-1-nonanol
1H,1H,11H-eicosafluoro-1-undecanol

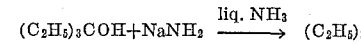
Of the suitable alcohols listed above, the alcohols with acyclic alkyl substituents on the beta carbon atom are preferred. Of these latter alcohols the ones indicated with an asterisk are more preferred.

Some of the hindered alcohols in which the beta carbon atom is completely substituted with alkyl groups are available commercially. The others can be prepared in the laboratory. The preparation of 2,2-dimethyl-1-hexanol is shown below:

PREPARATION OF 2,2-DIMETHYL-1-HEXANOL

1. Intermediate

(1) Sodium triethylmethoxide

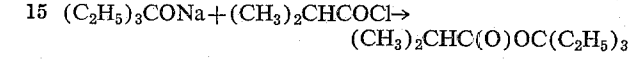


(2) Dimethylacetyl chloride



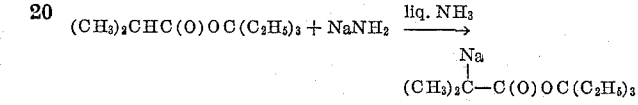
where C(O) is C=O

(3) Triethylcarbinyl isobutyrate

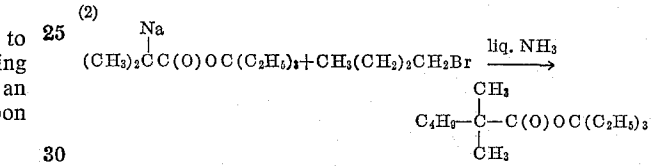


2. 2,2-dimethyl-1-hexanol

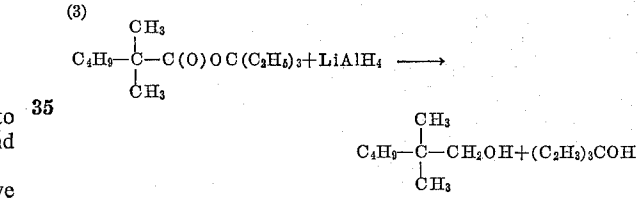
(1)



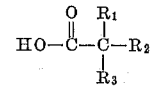
(2)



(3)



The hindered monobasic acids of our invention have the formula:

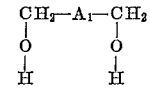


wherein R_1, R_2 and R_3 are acyclic alkyl groups containing from 1 to 18 carbon atoms. Examples of suitable hindered monobasic acids are the following:

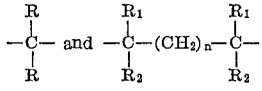
2,2-dimethyl-1-butanoic acid
2,2-dimethyl-1-pentanoic acid*
2,2-dimethyl-1-hexanoic acid*
2,2-dimethyl-1-heptanoic acid
2,2-dimethyl-1-octanoic acid*
2,2-dimethyl-1-nonanoic acid
2,2-dimethyl-1-decanoic acid*
2,2-dimethyl-1-hendecanoic acid
2,2-dimethyl-1-dodecanoic acid*
2,2-dimethyl-1-tetradecanoic acid*
2,2-dimethyl-1-hexadecanoic acid*
2,2-dimethyl-1-octadecanoic acid*
2,2-dimethyl-1-eicosanoic acid
2-methyl-2-ethyl-1-C_4-C_{20}-monocarboxylic acid
2-methyl-2-propyl-1-C_5-C_{20}-monocarboxylic acid
2-methyl-2-amyl-1-C_7-C_{20}-monocarboxylic acid
2,2-diethyl-1-C_4-C_{20}-monocarboxylic acid
2-ethyl-2-propyl-1-C_5-C_{20}-monocarboxylic acid
2-ethyl-2-butyl-1-C_6-C_{20}-monocarboxylic acid
2-ethyl-2-amyl-1-C_7-C_{20}-monocarboxylic acid
2,2-dipropyl-1-C_5-C_{20}-monocarboxylic acid
2-propyl-2-butyl-1-C_6-C_{20}-monocarboxylic acid
2-propyl-2-amyl-1-C_7-C_{20}-monocarboxylic acid
2,2-dibutyl-1-C_6-C_{20}-monocarboxylic acid
2,2-diamyl-1-C_7-C_{20}-monocarboxylic acid
2-butyl-2-amyl-1-C_7-C_{20}-monocarboxylic acid
2-hexyl-2-methyl-decanoic acid

Of the above suitable hindered monobasic acids the ones indicated with an asterisk are preferred.

The hindered polyhydroxy alcohols of our invention have the following formula:



wherein A_1 has a formula selected from the group consisting of:



wherein R, R_1 and R_2 are acyclic alkyl groups containing 1 to 4 carbon atoms and *n* is an integer varying from 1 to 10.

Examples of suitable hindered polyhydroxy alcohols are the following:

GLYCOLS

1,3-propanediols:
- 2,2-dimethyl*
- 2,2-diethyl*
- 2,2-dipropyl
- 2,2-dibutyl
- 2-methyl-2-ethyl*
- 2-methyl-2-propyl*
- 2-methyl-2-butyl*
- 2-ethyl-2-propyl
- 2-ethyl-2-butyl

1,6-hexanediols:
- 2,2,5,5-tetramethyl*
- 2,6-dimethyl-2,6-diethyl*
- 2,6-dimethyl-2,6-dipropyl
- 2,6-dimethyl-2,6-dibutyl
- 2,6-diethyl-2,6-dipropyl*
- 2,2,5,5-tetraethyl*
- 2,2,5,5-tetrabutyl
- 2,5,5-trimethyl-2-propyl-3-ethyl
- 2,2,5,5-tetramethyl-3,4-diethyl

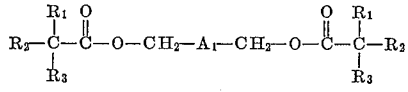
1,7-heptanediols:
- 2,4,6-trimethyl-2,6-dipropyl
- 2,2,4,6,6-pentamethyl-3-ethyl

1,8-octanediols:
- 2,7,7-trimethyl-2-propyl
- 2,2,4,5,7,7-hexamethyl
- 2,2,7,7-tetramethyl-3-ethyl
- 2,2,4,7,7-pentamethyl

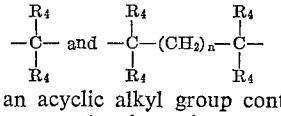
1,10-decanediols:
- 2,2,9,9-tetramethyl*

Of the above suitable hindered polyhydroxy alcohols the ones indicated with an asterisk are preferred.

Esters prepared from hindered monobasic acids and polyhydroxy alcohols have improved hydrolytic and thermal stability. These materials have the following formula:



wherein R_1 R_2 and R_3 are acyclic alkyl groups containing from 1 to 18 carbon atoms and where A_1 is selected from the group consisting of:



wherein R_4 is an acyclic alkyl group containing from 1 to 4 carbon atoms and *n* is an integer varying from 1 to 10.

Complex esters can be prepared from the hindered alcohols, hindered dibasic acids, and hindered polyhydroxy alcohols of the present invention. These complex esters possess improved hydrolytic stability. They can be shown diagrammatically as follows:

(A) A—B—A_1—B—A

where A equals hindered monohydroxy alcohol, B equals hindered dibasic acid, and A_1 equals hindered polyhydroxy alcohol; and

(B) D—A_1—B—A_1—D

where B equals hindered dibasic acid, A_1 equals hindered polyhydroxy alcohol, and D equals hindered monobasic acid.

The hindered dibasic acids per se which form an embodiment of our invention have been described previously.

Our invention relates also to the process for preparing the hindered alpha-substituted dibasic acids. This process can be described as comprising the following steps.

(a) Preparation of 2,2-dialkylacetyl halide,
(b) Preparation of alkali metal salt of trialkylcarbinol,
(c) Reaction of 2,2-dialkylacetyl halide with the alkali metal salt of trialkylcarbinol to form trialkylcarbinyl-2,2-dialkylacetate in presence of liquid ammonia,
(d) Preparation of sodio salt of trialkylcarbinyl-2,2-dialkylacetate by reaction with metallic sodium in liquid ammonia,
(e) Reaction of sodio salt of trialkylcarbinyl-2,2-dialkylacetate with an alkylene dihalide,
(f) Hydrolysis of product of step (e) to produce the 2,2,8,8-tetraalkyl substituted acid.

In a specific embodiment, the preparation of tetraethylazelaic acid comprises the following steps:

(*a*) *Synthesis of the intermediates*

(1) Preparation of diethylacetyl chloride:

$$(C_2H_5)_2CHC(O)OH + SOCl_2 \rightarrow (C_2H_5)_2CHC(O)Cl$$

(2) Preparation of sodium triethylmethoxide:

$$(C_2H_5)_3COH + NaNH_2 \xrightarrow{\text{liq. } NH_3} (C_2H_5)_3CONa$$

(3) Preparation of triethylcarbinyl 2-ethylbutyrate:

$$(C_2H_5)_2CHC(O)Cl + (C_2H_5)_3CONa \xrightarrow{\text{liq. } NH_3} (C_2H_5)CHC(O)OC(C_2H_5)_3$$

(*b*) *Synthesis of di(triethylcarbinyl) 2,2,8,8-tetraethylazelate*

(1) $$(C_2H_5)_2CHC(O)OC(C_2H_5)_3 + NaNH_2 \xrightarrow{\text{liq. } NH_3} (C_2H_5)_2\overset{Na}{C}COOC(C_2H_5)_3$$

$$(C_2H_5)_2\overset{Na}{C}C(O)OC(C_2H_5)_3 + BrCH_2CH_2CH_2CH_2CH_2Br \longrightarrow CH_2CH_2C(C_2H_5)_2C(O)OC(C_2H_5)_3$$
$$\vert$$
$$CH_2$$
$$\vert$$
$$CH_2CH_2C(C_2H_5)_2C(O)OC(C_2H_5)_3$$

(*c*) *Preparation of 2,2,8,8-tetraethylazelaic acid*

$$CH_2CH_2C(C_2H_5)_2C(O)OC(C_2H_5)_3$$
$$\vert$$
$$CH_2$$
$$\vert$$
$$CH_2CH_2C(C_2H_5)_2C(O)OC(C_2H_5)_3 \xrightarrow[HCl]{\text{dioxane}}$$

$$CH_2CH_2C(C_2H_5)_2COOH$$
$$\vert$$
$$CH_2$$
$$\vert$$
$$CH_2CH_2C(C_2H_5)_2COOH$$

While the purpose of this invention is to provide materials which are especially useful in the formulation of lubricants for use in turbojet and turboprop engines, the novel diesters herein described may find use in wide temperature range greases, high temperature heat transfer fluids, hydraulic fluids, and lubricants for precision instrument bearings. The novel diesters of this invention are

materials which provide hydrolytic stability to an extent hitherto unknown.

Conventional diesters were used as standards for comparison with the hindered diesters of this invention. Diisooctyl azelate, di-2-ethylhexyl sebacate, and diisobutyl azelate are commercially available diesters which were used per se. Di-2-ethylhexyl azelate is also commercially available, but the material used was purified by vacuum distilling, to obtain a center cut, and then filtering through alumina. Di-n-octyl azelate was prepared from commercially available materials. Its preparation is shown in the examples.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given. It is to be understood that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims.

Example I.—Preparation of di-n-octyl azelate

Materials	Moles	Grams
Azelaic acid	1	188.2
1-octanol	2.5	325.0
Toluenesulfonic acid		2.0
Benzene		(150 cc.)

Apparatus.—One-liter, three-necked, round-bottomed flask; Trubore stirrer; thermometer; Barrett water trap; reflux condenser; heating mantle; separatory funnel (two liters).

Procedure.—Charged 188.2 grams of azelaic acid, 325.0 grams of 1-octanol, 2.0 grams of toluenesulfonic acid, and 150 cc. of benzene to the reaction flask. Heat was applied and stirring commenced. Reflux initially was at 95° C. and continued for 8 hours, at which time the reflux temperature had risen to 110° C. During this period, 36 ml. of water was removed and collected in the water trap. The reaction mixture was then transferred to a separatory funnel and washed with 2 x 250 ml. portions of 5 percent aqueous sodium carbonate solution. It was then washed with 5 x 250 ml. portions of tap water until the pH (via Hydrion paper) was 7. The crude diester was dried over anhydrous magnesium sulfate and then filtered through a one-inch cake of Hyflo filter aid. The filter aid was washed with 100 ml. of benzene and the benzene was added to the product layer. The crude mixture (653 grams) was charged to a simple vacuum distillation setup. Using a water aspirator, benzene solvent was removed. Using a vacuum pump, a forecut which included excess alcohol was removed at 0.65 mm. Hg up to a vapor temperature of 187° C. At 0.07 mm. Hg 364.0 grams of diester (di-n-octyl azelate) was collected. A cut distilling between 202–235° C. at 0.17 mm. Hg weighed 18.2 grams. The bottoms weighed 7.5 grams. The diester cut was percolated through 104 grams of alumina. The filtrate had an acid number of 1.2 and a saponification number of 269. The acid number was further reduced to 0.02 by percolation through basic ion exchange resin.

Example II.—Preparation of di-2,2-dimethylhexyl azelate

Materials	Moles	Grams
2,2-dimethyl-1-hexanol [1]	1.1	141.8
Azelaic acid	0.56	104.5
Benzene (solvent and water entrainer)		(250 cc.)
p-Toluenesulfonic acid (catalyst)		2.0
Ether (wash solvent)		(650 cc.)

[1] Prepared in accordance with synthesis steps outlined in previous discussion.

Apparatus.—Two-liter, three-necked, round-bottom flask; Trubore stirrer; thermometer; Barrett water trap; water-cooled reflux condenser.

Procedure.—To the reaction flask were charged 141.8 grams of 2,2-dimethyl-1-hexanol, 104.5 grams of azelaic acid, 250 cc. of benzene, and 2 grams of p-toluenesulfonic acid. This mixture was heated with stirring at reflux for 8 hours, during which time 20.5 cc. of water was collected in the Barrett trap. In an additional 8 hours of heating at reflux with stirring, no additional water was collected. The reaction mixture was transferred to a separatory funnel and washed with 2 x 100 cc. portions of sodium carbonate solution which emulsified; but after standing overnight, it separated when 400 cc. of ether was added. This ethereal layer was then washed with 2 x 100 cc. portions of water, dried over calcium sulfate, and filtered through a three-inch cake (90 grams of alumina). The alumina was washed with 150 m. of ether. The ethereal filtrate and the ether wash of the alumina were combined and stripped of benzene and ether up to 100° C. on a water aspirator. At 0.14 mm. Hg using a vacuum fractionation setup, 163.4 grams of di-2,2-dimethylhexyl azelate was separated between 176–191° C. vapor temperature. A forecut (10 grams) and the still bottoms (14 grams) were also obtained. The yield of the diester based on the alcohol charged is 72.5 percent. The acid number of the distilled diester was 0.76. The acid number was reduced to 0.04 by percolation through basic ion exchange resin.

Example III.—Preparation of di-2,2-diethylbutyl azelate

Materials	Moles	Grams
2,2-diethyl-1-butanol [1]	0.95	121.5
Azelaic acid	0.475	89.4
Benzene		(250 cc.)
p-Toluenesulfonic acid		2.0
Ether		(650 cc.)

[1] Prepared in accordance with synthesis steps outlined in previous discussion.

Apparatus.—Same as in Example II.

Procedure.—The procedure was the same as used in Example II. A yield of 148.3 grams (76.5% of theory based on alcohol charged) of product was obtained. The boiling range of the product was 185–192° C. at 0.12 mm. of mercury. The distilled diester had an acid number of 0.97. The acid number was reduced to 0.02 by percolation through basic ion exchange resin.

Example IV.—Preparation of di-2,2-dimethylamyl azelate

Materials	Moles	Grams
Azelaic acid	0.5	94
2,2-dimethyl-1-pentanol	1.1	128
p-Toluenesulfonic acid		2
Benzene		(200 cc.)

Apparatus.—Same as in Example II.

Procedure.—Charged azelaic acid (94 grams), 2,2-dimethylpentanol (128 grams), toluenesulfonic acid (2 grams), and benzene (200 cc.) to the reaction flask. Heating and stirring were commenced, and at reflux (100–110° C.) water was collected. In eight hours 18.5 cc. of water was collected. The crude diester mixture was filtered through 185 grams of alumina. The alumina was washed with pentane and the pentane wash added to the diester filtrate. Pentane, benzene, and light ends were removed up to 166° C. pot temperature at 0.0 mm. Hg pressure. The stripped diester, diluted 50 percent by volume with pentane, was percolated through alumina and then a 12-inch column of the basic ion exchange resin (IR–45). Pentane was removed up to 100° C. at .1 mm. Hg. The acid number of this undistilled diester was 0.03. It weighed 170 grams (88.5 percent yield).

The second batch was prepared using the same procedure except that the diester was distilled. The di(2,2-dimethylamyl) azelate distilled between 160–180° C. at .1 mm. Hg pressure. The acid number of the dis-

tilled diester after percolating through basic ion exchange resin (IR–45) was 0.01. Over-all yield based on acid charged was 76 weight percent. Data on only the distilled diester are shown in the tables.

Example V.—Preparation of di-n-octyl-2,2,8,8-tetraethylazelate

(A) Preparation of 2,2,8,8-tetraethylazelaoyl chloride

Materials	Moles	Grams
2,2,8,8-tetraethylazelaic acid [1]	.282	84.7
Thionyl chloride	.643	76.7
Benzene (solvent)		(450 cc.)

[1] Prepared in accordance with synthesis steps outlined in previous discussion.

Apparatus.—Two-liter, three-necked flask; Trubore stirrer; reflux condenser; thermometer.

Procedure.—Charged 76.7 grams of thionyl chloride to the dry reaction flask along with 84.7 grams of 2,2,8,8-tetraethylazelaic acid and 450 cc. of benzene. Stirring was commenced and the mixture heated at 78° C. until hydrogen chloride gas evolution ceased (eight hours). The crude mixture was stripped of excess thionyl chloride and benzene at atmospheric pressure up to 122° C. pot temperature. On house vacuum at maximum pot temperature of 118° C., remaining traces of light ends were removed. The acyl halide bottoms which solidified on cooling weighed 92 grams (theoretical 95 grams). This product analyzed 17.5 percent Cl (theoretical 21).

(B) Preparation of di(n-octyl)-2,2,8,8-tetraethylazelate

Materials	Moles	Grams
Ferric nitrate (catalyst for amide preparation)		1.0
Ammonia (solvent and reactant)		(1000 cc.)
1-octanol	.988	128.5
Sodium	.988	22.7
Ether (solvent)		(2000 cc.)
2,2,8,8-tetraethylazelaoyl chloride	.494	166.2

Apparatus.—Two-liter, three-necked, round-bottomed flask; Trubore stirrer; Dry Ice-cooled condenser; bubble counter; drying tube; dropping funnel.

Procedure.—Charged 1,000 cc. of ammonia to the dry nitrogen-flushed reaction flask; then 0.5 gram of sodium metal was added. After the solution turned blue, the liquid was blown with dry air until the color was discharged; then 1.0 gram of ferric nitrate was added. Stirring was commenced, and the remaining 22.2 grams of sodium metal was added in small portions over a period of 2.0 hours. The temperature of the reaction flask was held at —35° C. Ten minutes after the addition of the sodium was completed, the blue color was discharged. To this mixture was added dropwise 128.5 grams of 1-octanol diluted with 300 cc. of dry ether. After the final addition of 1-octanol, an additional 200 cc. of dry ether was added. Ammonia was allowed to evaporate overnight; then nitrogen was blown through the pot mixture, which was heated on a steam bath for five hours. During this period, 500 cc. of ether was added. Next, 166.2 grams of 2,2,8,8-tetraethylazelaoyl chloride in 300 cc. of dry ether was added at such a rate as to maintain constant reflux and control the reaction. Post-stirring was continued for three hours. Ice water (500 cc.) was added cautiously over 30 minutes. The mixture was filtered to remove a small quantity of flocculent which hampered separation of the water and ether layers. The two layers were then separated and the ether wash of the aqueous layer was combined with the ether layer. The ether layer was washed with 2 x 200 cc. portions of 10 percent sodium hydroxide and finally with water until the wash water was neutral to "pHydrion" paper. The ether layer was filtered through a one-inch cake of Hyflo filter aid and dried over calcium sulfate. Ether was removed by heating to 60° C. at atmospheric pressure after filtering through 100 grams of alumina. The crude diester was charged to a vacuum distillation setup and stripped up to 200° C. at 0.1 mm. Hg pressure. The maximum vapor temperature during this period was 68° C. Overhead weighed 16.7 grams. The bottoms product weighed 232.5 grams. The product diester was diluted 50 percent by volume with pentane and percolated through 180 grams of alumina followed by a 12-inch column of basic ion exchange resin (IR–45). Both columns were flushed with pentane and the wash added to the effluent diester. Pentane was removed up to 110° C. at 0.1 mm. Hg pressure. The product diester weighed 177.5 grams. This product had an acid number of 0.02 and analyzed 75.0 percent carbon (theoretical 75.7) and 12.2 percent hydrogen (theoretical 12.2).

Example VI.—Preparation of di-2,2-dimethylamyl-2,2,8,8-tetraethylazelate

(A) Preparation of 2,2,8,8-tetraethylazelaoyl chloride

Materials	Moles	Grams
2,2,8,8-tetraethylazelaic acid [1]	0.513	154
Thionyl chloride	1.26	150
Benzene (solvent)		(500 cc.)

[1] Prepared in accordance with synthesis steps outlined in previous discussion.

Apparatus.—Two liter, three-necked flask; Trubore stirrer; reflux condenser; thermometer.

Procedure.—Charged 150 grams of thionyl chloride to the dry reaction flask along with 154 grams of 2,2,8,8-tetraethylazelaic acid in 500 cc. of benzene. Stirring was commenced, and the mixture was heated at 78° C. until hydrogen chloride gas evolution ceased (12 hours). The crude mixture was stripped of excess thionyl chloride and benzene at atmospheric pressure up to 125° C. pot temperature. On house vacuum at maximum pot temperature of 118° C., remaining traces of light ends were removed. The acyl halide bottoms weighed 170 grams (theoretical 174 grams).

(B) Preparation of di-(2,2-dimethylamyl)-2,2,8,8-tetraethylazelate

Materials	Moles	Grams
Ferric nitrate (catalyst for amide preparation)		1.0
Ammonia (solvent and reactant)		(1000 cc.)
2,2-dimethyl-1-pentanol	1	116
Sodium	1	23
Ether (solvent)		(1500 cc.)
2,2,8,8-tetraethylazelaoyl chloride	0.504	170

Apparatus.—Two liter, three-necked flask; Trubore stirrer; Dry Ice-cooled condenser; bubble counter; drying tube; dropping funnel.

Procedure.—Charged 1,000 cc. of ammonia to the dry nitrogen-flushed reaction flask; then 0.5 gram of sodium metal was added. After the solution turned blue, the liquid was blown with dry air until the color was discharged. One gram of ferric nitrate was added. Stirring was commenced, and the remaining 22.5 grams of sodium was added in small portions over a period of one hour. The temperature of the reaction flask was held at —35° C. Ten minutes after the addition of sodium was completed, the blue color was discharged. To this mixture was added dropwise 116 grams of 2,2-dimethylpentanol diluted with 300 cc. of dry ether. After the final addition of 2,2-dimethylpentanol, ammonia was allowed to evaporate overnight. Nitrogen was blown through the reaction mixture, which was heated on a steam bath for six hours. Two hundred cc. of ether was added followed by 170 grams of 2,2,8,8-tetraethylazelaoyl chloride in 300 cc. of dry ether at such a rate as to maintain constant reflux and control the reaction.

Poststirring was continued for three hours at full reflux. Ice water (750 cc.) was added cautiously over ½ hour. The mixture was filtered to remove fluocculent material and transferred to a separatory funnel in which two layers formed. The water layer was removed and washed with 200 cc. of ether and the ether wash combined with the ether layer. The ether layer was washed with water until the resulting water wash was neutral to pHydrion paper. The ether layer was dried overnight over calcium sulfate, filtered through alumina, and stripped of ether up to 60° C. at atmospheric pressure. The crude diester was charged to a vacuum distillation setup and stripped up to 192° C. at 0.25 mm. Hg pressure. The maximum vapor temperature was 23° C. The product diester (bottoms) was diluted 50 percent by volume with pentane and percolated through a 12-inch column of basic ion exchange resin (IR–45). The column was washed with pentane and the washings combined with the product-containing layer. Pentane was removed up to 115° C. at 0.3 mm. Hg pressure. The product weighed 198.5 grams. The acid number of the diester was 0.64.

TESTING PROCEDURES (EXAMPLES I–VI)

Thermal stability testing

The thermal stability of each of the esters prepared was determined using a simple test. A 25-ml. sample of the ester to be tested was charged to a tube 60 cm. long, 25 cm. in diameter, fitted with a side arm 8 cm. from the top of the tube to which was attached through a standard taper joint a U-tube containing mercury. The top of the test tube was fitted with a 24/40 standard taper joint in which was fitted a stopcock with an 8-mm. I.D. tube extending inside the test tube to with 10 cm. of the bottom. The stopcock was opened, nitrogen gas was introduced, and the testing tube flushed with the U-tube removed. The U-tube was then inserted, flushed with nitrogen, and a slight positive nitrogen pressure allowed to remain. The tube was immersed in an aluminum block bath and heated to 550° C. for 48 hours. The acid numbers were then determined by means of a Precision Automatic Titrator, using ASTM procedure D–664–54.

In calculating the percent decomposition, as shown in Table III, the saponification number was assumed to be equivalent to 100 percent decomposition.

Hydrolytic stability testing

Timed saponification numbers were made on both the reference diesters and the hindered diesters. The time intervals chosen were 0.5 hour, 2 hours, 4 hours, and 24 hours. The saponification numbers were determined using ASTM procedure D–939–54.

Physical tests

The various physical tests conducted used standard ASTM procedures.

TABLE I.—ANALYTICAL DATA ON HINDERED ALCOHOLS AND ACID OF EXAMPLES I–VI

	Melting point, ° C.	Boiling point, ° C.	Boiling point, ° C. (Literature)	Acid No.
Tetraethylzaelaic acid.	135–136			378–380 (calculated 380).
2,2-dimethyl-1-hexanol.		75–75 at 14 mm.[3]	80–82 at 14 mm. Hg[1]	
2,2-diethyl-1-butanol.		85–93 at 25 mm. Hg	92 at 25 mm. Hg[2]	

[1] JACS, 55, 1121 (1933).
[2] JACS, 78, 5416 (1956).
[3] Gauge not calibrated.

TABLE II—PHYSICAL PROPERTIES OF DIESTERS SHOWN IN EXAMPLES I–VI

Example Number	Diester	Viscosities			Viscosity index	ASTM slope	Density at 25° C.	Refractive index at 25° C., NaD
		Cs. at −40° F.	Cs. at 100° F.	Cs. at 210° F.				
	Conventional:							
	Diisooctyl azelate	1,285	12.54	3.38	164	0.686	0.9131	1.4488
	Di-2-ethylhexyl sebacate	1,400	12.80	3.34	154	0.706	0.9106	1.4492
	Diisobutyl azelate	254	5.58	1.90		0.802	0.9281	1.4348
I	Di-n-octyl azelate	Solid	11.32	3.25	175	0.674	0.9091	1.4472
	Di-2-ethylhexyl azelate	1,242	10.96	2.99	145	0.676	0.9135	1.4481
	Hindered:							
II	Di-2,2-dimethylhexyl azelate	4,722	15.90	3.65	133	0.725	0.9093	1.4471
III	Di-2,2-diethylbutyl azelate	8,343	21.03	4.43	1,414	0.700	0.9323	1.4555
IV	Di-2,2-dimethylamyl azelate (redistilled)	3,140	13.26	3.23	126	0.736	0.9151	1.4451
V	Di-n-octyl-2,2,8,8-tetraethyl azelate	Not run	43.27	6.33	104	0.736	0.9082	1.4560
VI	Di-2,2-dimethylamyl-2,2,8,8-tetraethyl azelate	Not run	118.60	8.62		0.832	0.9113	1.4545

TABLE III.—THERMAL STABILITY STUDIES (EXAMPLES I–VI)

[25 ml. sample heated in nitrogen atmosphere for 48 hours at 550° F.]

Example Number	Diester	Acid No.[1] (Before)	Acid No.[1] after—		Percent[2] decomposition		Saponification Number, mg. KOH/gm.
			Run No. 1	Run No. 2	Run No. 1	Run No. 2	
	Conventional:						
	Diisooctyl azelate	0.02	72	95	26.5	34.9	272
	Di-2-ethylhexyl sebacate	0.04	43	53	16.2	19.9	266
	Diisobutyl azelate	0.01	57	61	15.5	16.6	368
I	Di-n-octyl azelate	0.03	49	67	17.8	24.4	275
	Di-2-ethylhexyl azelate	0.07	47	40	17.3	14.8	271
	Hindered:						
II	Di-2,2-dimethylhexyl azelate	0.04	4.4	4.9	1.6	1.8	273
III	Di-2,2-diethylbutyl azelate	0.02	7.1	5.9	2.6	2.1	275
IV	Di-2,2-dimethylamyl azelate	0.01	13	13	4.4	4.4	296
V	Di-n-octyl-2,2,8,8-tetraethyl azelate	0.03	56		20.2		[3] 214
VI	Di-2,2-dimethylamyl-2,2,8,8-tetraethyl azelate	0.64	8		3.5		[3] 226

[1] Acid number in mg. KOH/gm.
[2] 100% decomposition is equal to saponification number.
[3] Theoretical.

TABLE IV.—HYDROLYTIC STABILITY STUDIES (EXAMPLES I-VI)

Example Number	Diester	Acid Number	Saponification Number, mg. KOH/gm.		2 hours	4 hours	24 hours
			Theoretical	Actual (30 minutes)			
	Conventional:						
	Diisooctyl azelate	0.02	272	272			
	Di-2-ethylhexyl sebacate	0.04	262	266			
	Diisobutyl azelate	0.01	334	368			
I	Di-n-octyl azelate	0.03	272	275			
	Di-2-ethylhexyl azelate	0.07	272	271			
	Hindered:						
II	Di-2,2-dimethylhexyl azelate	0.04	272	273			
III	Di-2,2-diethylbutyl azelate	0.02	272	275			
IV	Di-2,2-dimethylamyl azelate	0.01	292	296			
V	Di-n-octyl-2,2,8,8-tetraethyl azelate	0.03	214	18	25	22	33
VI	Di-2,2-dimethylamyl-2,2,8,8-tetraethyl azelate	0.64	226	19	19	21	76

Example VII.—Preparation of 2,2,8,8-tetraethylazelaic acid

(A) Preparation of 2-ethylbutyryl chloride

Materials	Mole weight	Moles	Quantity, g.
2-ethylbutyric acid	116.16	15	1,743
Thionyl chloride, Eastman grade	118.98	16.8	2,000

Procedure.—To 2000 grams of thionyl chloride maintained at 45° C., 2-ethylbutyric acid (1743 grams) was added dropwise. The mixture was then heated to 75° C. for four hours to drive out the remaining sulfur dioxide. The product (1685 grams, 83.5 percent) distilled at 135–137° C. through a six-inch vacuum jacketed column packed with glass helices.

(B) Preparation of triethylcarbinyl 2-ethylbutyrate

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia, anhydrous			2,000 cc.
Sodium, purified lump	22.997	6.1	140 g.
Triethylcarbinol, Eastman grade	116	6	696 g.
2-ethylbutyryl chloride	134.61	6	807 g.
Ether, anhydrous reagents			1,500 cc.

Procedure.—Sodium amide was prepared from 140 grams of sodium and 2 liters of liquid ammonia, using ferric nitrate as catalyst. Triethylcarbinol (969 grams) in 300 cc. of dry ether was slowly added to the reaction mixture. The ammonia was allowed to evaporate, and the mixture was refluxed in a stream of nitrogen for 12 hours. Approximately one liter of dry ether was added during this time.

A solution of 807 grams of 2-ethylbutyryl chloride in 200 cc. of ether was added dropwise to the reaction mixture. This was then stirred for one hour and heated under reflux for another hour. Water was added to dissolve the solids. The ethereal solution was washed with 10 percent sodium hydroxide, washed with water until neutral, and dried over calcium sulfate. Fractional distillation of the crude mixture yielded 1067 grams (83.5 percent) of triethylcarbinyl 2-ethylbutyrate (B.P. 102–105° C. at 10 mm.).

(C) Preparation of di-(triethylcarbinyl)2,2,8,8-tetraethylazelate

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia, anhydrous			2,000 cc.
Triethylcarbinyl 2-ethylbutyrate	214	5	1,067 g.
1,5-dibromopentane, Eastman grade	229.97	2.5	575 g.
Sodium, purified lump	22.997	5	155 g.
Ether, anhydrous reagent			600 cc.

Procedure.—Sodium amide was prepared from 115 grams of sodium and 2 liters of liquid ammonia. Triethylcarbinyl 2-ethylbutyrate (1067 grams) was added dropwise, and the mixture was stirred for 1.5 hours. A solution of 575 grams of dibromopentane in 200 cc. of ether was added dropwise, and stirring was continued for 1.5 hours. More ether (400 cc.) was added, and the ammonia was allowed to evaporate. After refluxing the solution one hour, water was added to dissolve the solids present. The ethereal solution was washed with water until neutral, dried over calcium sulfate, and reduced to small volume under vacuum. The crude residue weighing 1002 grams was hydrolyzed without further purification.

(D) Hydrolysis of di-(triethylcarbinyl)2,2,8,8-tetraethylazelate

Materials	Mole weight	Moles	Quantity
Di-(triethylcarbinyl)2,2,8,8-tetraethylazelate.	496	2.02	1,002 g.
Hydrochloric acid, concentrated reagent.	36.5	5.35	450 cc.
Dioxane, commercial			500 cc.

Procedure.—Concentrated hydrochloric acid (450 cc.) was slowly added to a refluxing solution of the crude di-(triethylcarbinyl) 2,2,8,8-tetraethylazelate in 500 cc. of dioxane. After refluxing for two hours, 945 cc. of azeotropic distillate had been collected. Water was added to precipitate the crude acid, which was collected on a filter, recrystallized twice from 90:10 ethanol-methanol and water and once from acetone-naphtha. The purified acid (M.P. 142–143.5° C.) obtained weighed 461.5 grams (61.5 percent, based on triethylcarbinyl 2-ethylbutyrate). Acid number: calculated for tetraethylazelaic acid, 374; found, 381.

Example VIII.—Preparation of 2-methyl-2-ethyl-1-pentanol

(A) Preparation of 2-methylpentanoyl chloride

Materials	Mole weight	Moles	Grams
2-methylpentanoic acid	116.16	10.7	1,242
Thionyl chloride	118.98	12.2	1,457.5

Procedure.—To 1457.5 grams of thionyl chloride in a dry nitrogen-flushed flask, 2-methylpentanoic acid (1242 grams) was added dropwise with stirring. The temperature was maintained at 35–45° C. After the addition was completed, the temperature was raised to 80° C. When gas evolution had ceased, the material was fractionated at atmospheric pressure. 2-methylpentanoyl

chloride (1176 grams, 82.5 percent) distilled at 137–139° C.

(B) Preparation of triethylcarbinyl 2-methylpentanoate

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia			2,000 cc.
Sodium	22.997	6.1	140 g.
Triethylcarbinol	116	6	696 g.
2-methylpentanoyl chloride	134.6	6.13	825 g.
Ether			3,000 cc.

Procedure.—To 2000 cc. of liquid ammonia in a dry nitrogen-flushed flask was added 0.5 gram of sodium metal. The blue color was discharged with a stream of dry air; then 1 gram of ferric nitrate was added. The remaining sodium (139.5 grams) was added in small portions with stirring. To this mixture was added a solution of 696 grams of triethylcarbinol in 500 cc. of dry ether. The ammonia was allowed to evaporate overnight, and the reaction mixture was then treated with a stream of nitrogen and heated under reflux for 15 hours, 1500 cc. of ether being added to the reaction flask during this time.

Next, a solution of 825 grams of 2-methylpentanoyl chloride in 200 cc. of ether was added dropwise over a 4-hour period. Stirring was continued for 1 hour. Water (1500 cc.) was slowly added. The contents of the flask were filtered, and the product was extracted with ether. The ether solution was washed with two 250-cc. portions of 10 percent sodium hydroxide and then with water until the wash water was neutral, dried over calcium sulfate, filtered, and freed of solvent at atmospheric pressure. The residue was vacuum fractionated. The product, triethylcarbinyl 2-methylpentanoate (930 grams; 72.5 percent) distilled at 92–101° C. at 10 mm. Hg.

(C) Preparation of triethylcarbinyl 2-methyl-2-ethylpentanoate

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia			2,000 cc.
Sodium	22.997	4.35	100 g.
Triethylcarbinyl 2-methylpentanoate	214	4.35	930 g.
Ethyl bromide	108.98	4.35	474 g.
Ether			2,000 cc.

Procedure.—To 2000 cc. of liquid ammonia in a dry nitrogen-flushed flask was added 1.0 gram of sodium. The blue color was discharged with a stream of dry air; then 1.0 gram of ferric nitrate was added. The remaining sodium (99 grams) was added in small portions with stirring. To this mixture, triethylcarbinyl 2-methylpentanoate (930 grams) was added dropwise. Stirring was continued for two hours after the addition was completed. Next, a solution of 474 grams of ethyl bromide in 300 cc. of ether was added dropwise. The ammonia was allowed to evaporate, and ether (1100 cc.) was added to facilitate stirring. Sufficient water (about 1500 cc.) was added to dissolve the solids formed. The contents of the flask were filtered, and the product was taken up into ether. The ether solution was washed with water until neutral, dried over calcium sulfate, filtered, and freed of solvent at atmospheric pressure. The residue was fractionated. The overhead temperature was taken to 115° C. at 12 mm. Hg. The residue (705 grams) was reduced to the alcohol without further treatment.

(D) Reduction of triethylcarbinyl 2-methyl-2-ethylpentanoate to 2-methyl-2-ethylpentanol

Materials	Mole weight	Moles	Quantity
Lithium aluminum hydride	37.94	2.63	100 g.
Ether			1,000 cc.
Triethylcarbinyl 2-methyl-2-ethylpentanoate.	242	2.9	705 g.

Procedure.—A mixture of 100 grams of lithium aluminum hydride and 1000 cc. of dry ether in a dry nitrogen-flushed flask was stirred and heated under reflux for 5 hours using a steam bath. Triethylcarbinyl 2-methyl-2-ethylpentanoate (705 grams) was added dropwise to the reaction mixture. Following the final ester addition, the mixture was refluxed for 16 hours. Water was added very slowly until hydrogen evolution ceased; then 50 percent H_2SO_4 was added until the solution was acidic. Additional water had to be added to complete solution of the solids in the flask.

The product was taken up into ether, washed with two 300-cc. portions of 10 percent sodium hydroxide and with water until neutral, dried over calcium sulfate, filtered, and freed of solvent at atmospheric pressure. The residue was vacuum fractionated. Triethylcarbinol weighing 80.4 grams distilled at 76–82° C. at 48 mm. Hg. 2-methyl-2-ethyl-1-pentanol (345 grams; 65 percent) distilled at 80–90° C. at 25 mm. Hg.

Example IX.—Preparation of di-(2-methyl-2-ethylpentyl)2,2,8,8-tetraethylazelate

Preparation of 2,2,8,8-tetraethylazelayl chloride

Materials	Mole weight	Moles	Quantity
2,2,8,8-tetraethylazelaic acid	300	.522	156.5 g.
Thionyl chloride, Eastman grade	118.98	1.31	156.5 g.
Benzene, ACS reagent			200 cc.
Pyridine, reagent			2 drops.

Procedure.—A mixture of 156.5 grams of 2,2,8,8-tetraethylazelaic acid, 156.5 grams of thionyl chloride, 200 cc. of benzene, and 2 drops of pyridine was heated to 45° C. for one hour and then at reflux for two hours. The benzene and thionyl chloride were distilled from the reaction mixture, finally heating to 150° C. and using moderate vacuum to remove the remaining volatile materials. The residue was used in the following reaction without further treatment.

Acylation of 2-methyl-2-ethylpentanol with 2,2,8,8-tetraethylazelayl chloride

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia			1,500 cc.
2-methyl-2-ethylpentanol	130	1.88	245 g.
2,2,8,8-tetraethylazelayl chloride	337	.94	
Ether			2,500 cc.
Sodium	22.997	1.88	43.2 g.

Procedure.—To 1500 cc. of liquid ammonia in a dry nitrogen-flushed flask was added 0.5 gram of sodium metal. The blue color was discharged with a stream of dry air; then 1 gram of ferric nitrate was added. The remaining sodium (42.7 grams) was added in small portions with stirring over a two-hour period. To the sodium amide mixture a solution of 245 grams of 2-methyl-2-ethylpentanol in 400 cc. of dry ether was added slowly. The ammonia was allowed to evaporate overnight. The mixture was refluxed for eight hours while a stream of nitrogen was passed through it, 500 cc. of dry ether being added to the reaction mixture during this time. Next, the tetraethylazelayl chloride prepared from 0.94 mole of

acid was dissolved in 500 cc. of dry ether and added dropwise to the reaction mixture at such a rate as to maintain constant reflux. This was then refluxed for one hour, and water (1500 cc.) was added. The contents of the flask were filtered, and the product was taken up into ether, washed with two 250-cc. portions of 10 percent sodium hydroxide and with water until neutral, dried over calcium sulfate, filtered through Hyflo, and freed of solvent at atmospheric pressure. Volatile materials were removed by heating the mixture to 195° C. (vapor temperature: 88° C.) at 0.5 mm. Hg pressure. The product ester was the residue (436.5 grams; 89 percent).

The residue was refluxed for two hours with 400 cc. of 0.5 N alcoholic potassium hydroxide. The temperature of the reaction mixture was about 78° C. Next, pentane and water were added, and the organic layer was washed with water until neutral, filtered through Hyflo, and reduced to small volume using a water aspirator. The infrared spectrum of the sample showed that it was free of anhydride. Acid number of the product was 0.32. In order to reduce the acid number, the ester was diluted with pentane and percolated through a 12-inch column of basic Amberlite IR–45. The pentane was removed by heating to 120° C. under oil pump vacuum. After filtering through a small inch-thick cake of Hyflo, the ester was still slightly hazy. It was dried over calcium sulfate for several days and filtered again. The product weighed 340 grams and had an acid number of 0.16. After another treatment with IR–45, the acid number was 0.04. Gas-liquid partition chromatography indicated that the major component comprised 79.4 percent of the sample.

Example X.—Preparation of di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate

Materials	Mole weight	Moles	Quantity
2,2-dimethylhexanol-1	130	4.62	600 g.
Tetraethylazelayl chloride	337	[1] 0.75	
Ether			500 cc.
Sodium	22.997	1.52	35 g.

[1] Theory.

Procedure.—To 600 grams of refluxing 2,2-dimethylhexanol-1 in a dry flask, sodium (35 grams) was added in small portions over a period of 2.5 hours. The mixture was refluxed for one hour, and then a solution of 0.75 mole of crude tetraethylazelayl chloride in 300 cc. of dry ether was added dropwise. The temperature of the reaction mixture remained at 70–80° C. during the acid chloride addition without external heating. Refluxing was continued for two hours after the addition. Enough water was added to dissolve the solids formed. The product was taken up in ether, washed twice with 250 cc. of aqueous 10 percent sodium hydroxide and by water until neutral, dried over calcium sulfate, and reduced to small volume at atmospheric pressure. Remaining volatile materials were then removed by heating to 200° C. at 0.5 mm. Hg pressure. Weight of the residue was 378 grams (96 percent).

The ester was refluxed for two hours with 0.5 N alcoholic potassium hydroxide. The base was washed from the ester and the ester dried over calcium sulfate. Acid number of the product was 0.23. This was percolated through Amberlite IR–45, which reduced the acid number to 0.01. The infrared spectrum indicated the absence of anhydride. Gas-liquid partition chromatography furnished an assay of 91.5 percent.

Example XI.—Preparation of di-(2,2-dimethyloctyl)2,2,8,8-tetraethylazelate

This product was prepared by the same procedure as used in Example X.

Example XII.—Preparation of di-(2,2-dimethyldecyl)2,2,8,8-tetraethylazelate

This product was prepared by the same procedure as used in Example X.

Example XIII.—Preparation of di-(2,2-dimethylhexyl)2,2,6,6-tetramethylpimelate

2,2,6,6-tetramethylpimelic acid was prepared by a procedure similar to that used in Example VII.

The ester was prepared by a procedure similar to that used in Example IX.

Example XIV.—Preparation of 2,8-dimethyl-2,8-dipropylazelaic acid

(A) Preparation of di-(triethylcarbinyl)2,8-dimethyl-2,8-dipropylazelate

Materials	Mole weight	Moles	Quantity
Ferric nitrate			1 g.
Ammonia, anhydrous			2,000 cc.
Triethylcarbinyl 2-methylpentanoate	214	5	1,072 g.
1,5-dibromopentane, Eastman grade	229.96	2.5	575 g.
Sodium, purified lump	22.997	5	115 g.
Ether, anhydrous reagent			1,000 cc.

Procedure.—Sodium amide was prepared from 115 grams of sodium and 2 liters of liquid ammmonia using ferric nitrate as catalyst. Triethylcarbinyl 2-methylpentanoate (1072 grams) was added dropwise, and the mixture was stirred for two hours. A solution of 575 grams of 1,5-dibromopentane and 500 cc. of ether was added dropwise, and stirring was continued for one hour following the addition. Allowing the ammonia to evaporate overnight resulted in loss of part of the reduction mixture through foaming. The mixture was heated for one hour to expel remaining ammonia, and sufficient water was added to dissolve the solids in the flask. The product was taken up into ether, washed with water until neutral, and dried over calcium sulfate. The solution was filtered and freed of solvents by distillation at atmospheric pressure. Distillation at 10 mm. pressure yielded 103 grams at 40–95° C. and 106 grams of triethylcarbinyl 2-methylpentanoate at 97–101° C. The crude product (residual) weighed 882.5 grams and was hydrolyzed without further purification.

(B) Hydrolysis of di-(triethylcarbinyl)2,8-dimethyl-2,8-dipropylazelate

Materials	Mole weight	Moles	Quantity
Di-(triethylcarbinyl)2,8-dimethyl-2,8-dipropylazelate.	496	1.78	882.5 g.
Hydrochloric acid, concentrated reagent.	36.5		400 cc.
Dioxane, commercial			500 cc.

Procedure.—To a refluxing solution of 882.5 grams crude di-(triethylcarbinyl)2,8-dimethyl-2,8-dipropylazelate in 500 cc. of dioxane was slowly added concentrated hydrochloric acid (400 cc.). After refluxing two hours, azeotropic distillate was collected which separated into about 700 cc. of an olefinic layer and 280 cc. of dioxane. Additional dioxane (250 cc.) was added to the reaction mixture. The contents of the flask were then poured into two liters of water, and the oily product was allowed to crystallize overnight. The solid was collected on a filter, washed with pentane to remove color, recrystallized from aqueous 90:10 ethanol-methanol, and washed with pentane. Three crops were obtained. The

pentane washings contained the brown impurities were reduced in volume on the steam bath and were allowed to stand for several days. The resulting crystalline mass was washed with pentane, filtered, and dried. The total yield of 2,8-dimethyl-2,8-dipropylazelaic acid was 450 grams, representing 60 percent of the theoretical amount based on 1,5-dibromopentane. Melting range on each crop was 95–110° C. Infrared spectra showed that the crops were essentially identical with one another. Acid No.: calculated, 374; found, 375.

Example XV.—Preparation of di-(2,2-dimethylhexyl) 2,8-dimethyl-2,8-dipropylazelate

This product was prepared from 2,2-dimethylhexanol and the acid prepared in Example XIV by a procedure similar to that used in Example IX.

Example XVI.—Preparation of 2,8-dimethyl-2,8-diethylazelaic acid

This material was prepared by a procedure similar to that used in Examples VII and XIV.

Example XVII.—Preparation of di-(2,2-dimethylhexyl) 2,8-dimethyl-2,8-diethylazelate

This product was prepared from 2,2-dimethylhexanol and the acid prepared in Example XVI by a procedure similar to that used in Example IX.

Example XVIII.—Preparation of di-(1H,1H,7H-dodecafluoro-1-heptyl)2,2,8,8-tetraethylazelate

Materials	Mole weight	Moles	Quantity
2,2,8,8-tetraethylazelayl chloride	337	[1] 1	337 g.[2]
Pyridine	79.1	1.45	115 g.
C7 Fluoroalcohol	332	1.43	477.5 g.
Benzene, ACS reagent			350 cc.

[1] Estimated. [2] Theory.

Procedure.—A mixture of 115 grams of pyridine and 100 cc. of benzene was slowly added to a solution of the crude 2,2,8,8-tetraethylazelayl chloride and 150 cc. of benzene. After refluxing for one hour, a mixture of 447.5 grams of C7 fluoroalcohol and 100 cc. of benzene was added slowly. The temperature was maintained at approximately 75° C. during the addition. The reaction mixture was then refluxed for three hours. A crystalline material formed in the flask during this time. Sufficient water was added to dissolve the solids present, and sufficient pentane was added to cause the organic layer to float. The organic layer was washed with dilute hydrochloric acid, water, and 10 percent sodium hydroxide. A large amount of a heavy red liquid settled to the bottom of the separatory funnel with each sodium hydroxide washing. This lower layer, weighing 261 grams, was found to be the fluoroalcohol. When no more fluoroalcohol separated during the sodium hydroxide washing, the organic layer was washed with water until neutral, and dried. An attempt was made to distill the solvents and other volatile materials from the crude ester, but copious acidic fumes were evolved. The crude ester was then filtered through alumina, but acid fumes were evolved again when the product was heated to 195° C. under 0.75 mm. pressure. The infrared spectrum indicated presence of considerable anhydride.

After treating three timess with dilute methanolic potassium hydroxide, the infrared spectrum showed no anhydride. The acid number was 0.67, but it had not proved susceptible of reduction by the base treatment. Gas-liquid partition chromatography furnished an assay of 95.8 percent.

Example XIX.—Preparation of di-(2,2-dimethyloctyl) 3,3-dimethylglutarate

This product was prepared from commercially available 2,2-dimethyloctanol and 3,3-dimethylgultaric acid by a procedure similar to that used in Example IX.

Example XX.—Preparation of di-(2,2-dimethylhexyl) 3,3,6,6-tetramethylsuberate

This product was prepared by the following general procedure:

(1) 3,3-dimethylglutaric anhydride was prepared from 3,3-dimethylglutaric acid,
(2) 3,3-dimethylglutaric anyhdride was converted to methyl hydrogen 3,3-dimethylglutarate,
(3) Dimethyl 3,3,6,6-tetramethylsuberate was prepared from methyl hydrogen 3,3-dimethylglutarate,
(4) Dimethyl 3,3,6,6-tetramethylsuberate was transesterified with 2,2-dimethylhexanol to form di-(2,2-dimethylhexyl)3,3,6,6-tetramethylsuberate.

Example XXI.—Preparation of 2-methyl-2-ethyl-1,3-propanediol di-(2,2-diethylpentanoate)

(A) Preparation of 2,2-diethylpentanoic acid

2,2-diethylpentanol was converted to 2,2-diethylpentanoic acid according to the procedure of J. Kenyon and B. C. Platt (J. Chem. Soc., 633, 1939). Yields of 53 and 48 percent were obtained. A typical preparation was as follows:

Materials	Mole weight	Moles	Quantity, g.
2,2-diethylpentanol-1	144	1	144
NaOH analytical reagent	40	0.75	30
$KMnO_4$ analytical reagent	158	2.15	340
SO_2, commercial			

Procedure.—Potassium permanganate (340 grams) in 3000 cc. of water was added slowly to a well-stirred mixture of 144 grams 2,2-diethylpentanol and 30 grams sodium hydroxide dissolved in 250 cc. of water. After twelve hours, the heat of reaction had dissipated. The mixture was then heated to 100° C. for one hour. Gaseous sulfur dioxide was introduced into the solution until it was acidic and the manganese dioxide went into solution. The organic layer formed was taken up in ether, washed well with water, and dried over Drierite. The filtered solution yielded 84 grams of 2,2-diethylpentanoic acid, distilling at 133–137° C. at 17 mm. Hg pressure. The yield was 53 percent, based on alcohol. Acid number: calculated, 354; observed, 348.

(B) Preparation of 2,2-diethylpentanoyl chloride

Materials	Mole weight	Moles	Quantity
2,2-diethylpentanoic acid	158	1.08	170 g.
Thionyl chloride, practical	118.98	2	238 g.
Pyridine, purified		2	2 drops.

Procedure.—To a mixture of 238 grams of thionyl chloride and 2 drops of pyridine, maintained at 40° C., 2,2-diethylpentanoic acid (170 grams) was added dropwise. After completing the addition, the mixture was heated under reflux for two hours. The thionyl chloride was distilled off at atmospheric pressure. 2,2-diethylpentanoyl chloride (172 grams, 90.5 percent) distilled at 95–97° C. at 30 mm. pressure.

(C) Acylation of 2-methyl-2-ethyl-1,3-propanediol with 2,2-diethylpentanoyl chloride

Materials	Mole weight	Moles	Quantity
Diethylpentanoyl chloride	176	0.98	172 g.
2-methyl-2-ethyl-1,3-propanediol	118	.425	50 g.
Pyridine, purified			200 cc.

Procedure.—2,2-diethylpentanoyl chloride (172 grams) was slowly added to a mixture of 200 cc. of pyridine and 50 grams of 2-methyl-2-ethyl-1,3-propanediol. The reaction mixture was externally heated during the addition, and solid began forming at 88° C. It was then heated to 100° C. for three hours. Methanol (20 cc.) was added, and the mixture was stirred for one hour. Water was added, and the product was taken up in ether, washed with dilute hydrochloric acid, washed with water until neutral, dried over Drierite, and distilled. The 2-methyl-2-ethyl-1,3-propanediol di-(2,2-diethylpentanoate), weighing 140.5 grams, distilled at 140–147° C. at 0.05 mm. The yield was 83 percent, based on alcohol. Gas-liquid partition chromatography indicated that the ester was 90.1 percent homogeneous.

Example XXII.—Preparation of 2-methyl-2-ethyl-1,3-propanediol di-(2-ethyl-2-isopropylhexanoate)

This product was prepared by the following general procedure:

(1) 2-ethylhexanoyl chloride was prepared from 2-ethylhexanoic acid,
(2) Triethylcarbinyl 2-ethylhexanoate was prepared from 2-ethylhexanoyl chloride and triethylcarbinol,
(3) Triethylcarbinyl 2-ethyl-2-isopropylhexanoate was prepared from triethylcarbinyl 2-ethylhexanoate and isopropyl bromide,
(4) Triethylcarbinyl 2-ethyl-2-isopropylhexanoate was hydrolyzed to form 2-ethyl-2-isopropyl hexanoic acid,
(5) 2-ethyl-2-isopropyl hexanoic acid was converted to the chloride,
(6) 2-methyl-2-ethyl-1,3-propanediol was acylated with e-ethyl-2-isopropylhexanoyl chloride to form the product.

In the examples the expression "GLPC" refers to gas liquid partition chromatography. This analytical technique is adequately described in either of the following publications:

Analysts, 77, 1952, pages 915–932, or
Petroleum Refiner, November 1955, pages 165–169.

In addition to the data shown, infrared spectra were determined on the various esters.

TESTING PROCEDURES (EXAMPLES VII–XXVII

Thermal stability in glass (copper present)

A 20-gram sample of the ester is placed in a tube 60 cm. long and 2.5 cm. in diameter and fitted with a side arm 8 cm. from the top of the tube to which is attached through a standard taper joint a U-tube containing mercury. At the top of the test tube is a 24/40 standard taper joint to which is fitted a stopcock with an 8 mm. I.D. tube extending inside the test tube to within 10 cm. of the bottom. The stopcock is opened, and the testing tube is flushed with nitrogen, leaving a slight positive pressure. The tube is immersed in an aluminum block bath and heated to 600° F. for 48 hours. The weight loss due to volatility, the percent viscosity change, and the acid number increase are noted. Percentage decomposition is calculated from the acid number increase, using the theoretical saponification number as representative of 100 percent decomposition. The test was conducted in the presence of a 1 by 6 cm. copper strip. The weight change of the copper is determined.

Thermal stability in steel

A 20-ml. sample of the ester is placed in a cylinder 7 inches long made from three-quarter-inch stainless steel tubing. A gauge is attached for pressure reading. The bomb is sealed under one atmosphere of nitrogen and immersed in an aluminum block bath for 6 hours at 600° F. (316° C.). The gauge pressure during the test and after cooling, the percentage viscosity change, and the acid number increase are obtained. Percentage decomposition is calculated from the acid number increase using the theoretical saponification number as representative of 100 percent decomposition.

Hydrolytic stability

Hydrolytic stability was determined by means of saponification number. The saponification number obtained on the sample was compared to the theoretical saponification number.

The procedure used a 2 hour reflux of the ester sample in alcoholic KOH. ASTM procedure D–94 was employed.

Physical tests

The various physical tests employed ASTM procedures.

TABLE V.—PHYSICAL PROPERTIES OF ESTERS IN EXAMPLES VII-XXII

Ester	Pour point, ° F.	Kinematic viscosity (cs.)			ASTM slope	Flash point, ° F.
		−40° F.	100° F.	210° F.		
Di-(2-methyl-2-ethylpentyl)2,2,8,8-tetraethylazelate	−20	(1)	144.3	9.50	0.847	465
Di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate	−25	(1)	106.1	8.47	0.830	450
Di-(2,2-dimethyloctyl)2,2,8,8-tetraethylazelate	−40	(1)	93.91	8.82	0.776	460
Di-(2,2-dimethyldecyl)2,2,8,8-tetraethylazelate	−45	(1)	112.7	10.51	0.742	495
Di-(2,2-dimethylhexyl)2,2,6,6-tetramethylpimelate	−60	44,822	20.56	3.71	0.813	380
Di-(1H,1H,7H-dodecafluoro-1-heptyl)2,2,8,8-tetraethylazelate	−20	----------	105.47	7.27	0.900	----------
Di-(2,2-dimethyloctyl)3,3-dimethylglutarate	−65	13,282	20.83	3.93	0.775	----------
Di-(2,2-dimethylhexyl)3,3,6,6-tetramethylsuberate	−65	30,000	41.13	5.55	0.790	(1)
Di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-diethylazelate	−25	(1)	52.48	5.87	0.842	(1)
Di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-dipropylazelate	−40	(1)	69.64	6.67	0.842	(1)
2-methyl-2-ethyl-1,3-propanediol di-(2-2,diethylpentanoate)	−40	(1)	32.98	4.43	.852	(1)
2-methyl-2-ethyl-1,3-propanediol di-(2-ethyl-2-isopropylhexanoate)	−40	(1)	109.4	7.97	.862	(1)

[1] Data not obtained.

TABLE VI.—ADDITIONAL PHYSICAL PROPERTIES AND ANALYSIS ON ESTERS OF EXAMPLES VII–XXII

Ester	Density (g./cc.), 25° C.	n_{D25}	Percent carbon		Percent hydrogen	
			Calculated	Found	Calculated	Found
Di-(2-methyl-2-ethylpentyl)2,2,8,8-tetraethylazelate	0.9133	1.4580	75.6	75.78	12.2	12.30
Di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate	0.9051	1.4550	75.6	75.57	12.2	12.23
Di-(2,2-dimethyloctyl)2,2,8,8-tetraethylazelate	0.8988	1.4559	(1)	(1)	(1)	(1)
Di-(2,2-dimethyldecyl)2,2,8,8-tetraethylazelate	0.8946	1.4579	77.3	77.21	12.6	12.43
Di-(2,2-dimethylhexyl)2,2,6,6-tetramethylpimelate	0.8999	1.4445	(1)	(1)	(1)	(1)
Di-(1H,1H,7H-dodecafluoro-1-heptyl) 2,2,8,8-tetraethylazelate	1.3234	1.3935	40.1	42.43	3.91	4.88
Di-(2,2-dimethyloctyl)3,3-dimethylglutarate	0.9012	1.4478	73.7	73.79	11.8	11.73
Di-2,2-dimethylhexyl)3,3,6,6-tetramethyl suberate	0.9074	1.4513	74.0	74.29	11.9	11.90
Di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-diethylazelate	0.9008	1.4506	75.0	75.03	12.1	11.99
Di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-dipropylazelate	0.8963	1.4513	75.6	75.45	12.2	12.24
2-methyl-2-ethyl-1,3-propanediol di-(2,2-diethylpentanoate)	0.9290	1.4509	72.4	72.75	11.6	11.86
2-methyl-2-ethyl-1,3-propanediol di-(2-ethyl-2-isopropylhexanoate)	0.9349	1.4610	74.01	74.20	11.98	12.05

[1] Data not obtained.

TABLE VII.—HYDROLYTIC STABILITY DATA ESTERS OF EXAMPLES VII–XXII

Ester	ASTM saponification number [1]		Percent decomposition [3]
	Observed	Theoretical [2]	
Di-(2-methyl-2-ethylpentyl)2,2,8,8-tetraethylazelate	5.3	214	2.5
Di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate	1.6	214	.75
Di-(2,2-dimethyloctyl)2,2,8,8-tetraethylazelate	2.7	193	1.4
Di-(2,2-dimethyldecyl)2,2,8,8-tetraethylazelate	8.3	176	4.7
Di-(2,2-dimethylhexyl)2,2,6,6-tetramethylpimelate	54	255	21.2
Di-(1H,1H,7H-dodecafluoro-1-heptyl)2,2,8,8-tetraethylazelate	57.2	116	49.3
Di-(2,2-dimethyloctyl)3,3-dimethylglutarate	251	255	98.5
di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-diethylazelate	1.41	226	0.6
Di-(2-2-dimethylhexyl)2,8-dimethyl-2,8-dipropylazelate	4.86	214	2.3
Di-(2,2-dimethylhexyl)3,3,6,6-tetramethyl suberate	156.2	247	63.3
2-methyl-2-ethyl-1,3-propanediol di-(2,2-diethylpentanoate)	0	282	0
2-methyl-2-ethyl-1,3-propanediol di-(2-ethyl-2-isopropylhexanoate)	0	247	0

[1] ASTM method D-94.
[2] For complete saponification.
[3] Percent decomposition=100 (observed saponification number)/theoretical saponification number).

TABLE VIII.—DATA ON THERMAL STABILITY IN GLASS (COPPER PRESENT) [1] ESTERS OF EXAMPLES VII–XXII—SECTION 1

Ester	Viscosity at 100° F. (cs.)			Acid number increase	Percent decomposition [2]
	Original	Final	Percent change		
Di-("iso-octyl") azelate	12.58	21.07	+67.6	120	44
Di-(2-ethylhexyl) sebacate	12.59	10.72	−14.9	46	17.5
Di-(2,2,4-trimethylpentyl) azelate	13.29	11.59	−12.8	9.5	3.5
Di-(2,2-dimethylhexyl) azelate	15.60	14.09	−4.5	6.2	2.3
Di-(2,2-dimethyloctyl) azelate	21.61	19.65	−9.0	7.7	3.2
Di-(2-methyl-2-ethylpentyl)2,2,8,8-tetraethylazelate	144.3	141.1	−2.2	13	6.1
Di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate	106.1	95.85	−9.9	6.1	2.8

[1] A 20-g. sample is maintained at 600° F. (316° C.) for 48 hours under nitrogen.
[2] Percentage decomposition=100 (acid number increase)/(theoretical saponification number).

TABLE VIII.—DATA ON THERMAL STABILITY IN GLASS (COPPER PRESENT) [1] ESTERS OF EXAMPLES VII–XXII—SECTION 2

Ester	Viscosity at 100° F. (cs.)			Acid number increase	Percent decomposition [2]
	Original	Final	Percent change		
Di-(2,2-dimethyloctyl)2,2,8,8-tetraethylazelate	93.91	100.7	+7.23	9.41	4.9
Di-(2,2-dimethylhexyl)2,2,6,6-tetramethylpimelate	20.56	20.86	+1.46	4.76	1.9
Di-(1H,1H,7H-dodecafluoro-1-heptyl) azelate	26.75	26.85	+0.4	2.86	2.1
Di-(1H,1H,7H-dodecafluoro-1-heptyl)2,2,8,8-tetraethylazelate	105.47	80.09	23.5	5.25	4.5
Di-(2,2-dimethyloctyl)3,3-dimethylglutarate	20.83	18.11	−13.1	1.7	0.67
Di-(2,2-dimethylhexyl)2,8-dimethyl-2,8-diethylazelate	52.48	44.61	−15.0	3.79	1.7
Di-(2,2-dimethylhexyl)3,3,6,6-tetramethyl suberate	41.13	25.88	−37.1	4.33	1.8

[1] A 20-g. sample is maintained at 600° F. (316° C.) for 48 hours under nitrogen.
[2] Percentage decomposition=100 (acid number increase)/(theoretical saponification number).

TABLE IX.—DATA ON THERMAL STABILITY IN STEEL PRESSURE CYLINDER [1] ESTERS OF EXAMPLES VII-XXII

Ester	Viscosity at 100° F. (cs.)			Acid number increase	Percent decomposition [2]
	Original	Final	Percent change		
Di-(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate	106.1	99.84	−5.9	3.4	1.6
Di-(2,2-dimethylhexyl)3,3,6,6-tetramethyl suberate	41.13	40.85	−0.7	1.3	0.5
Di-(2,2-dimethyloctyl)3,3-dimethylglutarate	20.83	19.51	−6.3	2.1	0.8
Di-(1H,1H,7H-dodecafluoro-1-heptyl)2,2,8,8-tetraethylazelate	105.45	93.27	−11.6	2.8	2.4
Di-(isooctyl) azelate	12.58	10.94	−13.0	32.4	11.9
Di-(2-ethylhexyl) sebacate	12.59	11.63	−7.6	30.2	11.5
Di-(2,2-diethylpentyl) azelate	25.32	11.96	−52.8	58.1	22.8
2-methyl-2-ethyl-1,3-propanediol di-(2,2-diethylpentanoate)	32.98	31.91	−3.2	5.4	1.9

[1] A 20-ml. sample is maintained at 600° F. (316° C.) for six hours under nitrogen.
[2] Percentage decomposition=100 (acid number increase)/(theoretical saponification number).

TABLE X.—PHYSICAL PROPERTIES—ESTERS OF EXAMPLES XXIII-XXVII

	Viscosity in centistokes			ASTM slope	Pour point, ° F.	Flash point, ° F.
	−40° F.	100° F.	210° F.			
2,2-dimethylvalerates:						
2-ethyl-2-butyl-1,3-propanediol	10,610	13.41	2.87	0.82	−65	330
2,2,5,5-tetramethyl-1,6-hexanediol	20,280	17.72	3.48	0.80	−70	345
2-methyl-2-ethylhexanoates:						
2-methyl-2-propyl-1,3-propanediol		23.88	3.67	0.87	−60	375
2,2,5,5-tetramethyl-1,6-hexanediol		46.15	5.22	0.86	−60	380
2-2-dimethyltetradecylate: 2-methyl-2-propyl-1,3-propanediol	[1] 10,616	36.82	6.35	0.69	−55	485

[1] Viscosity at −30° F.

TABLE XI.—THERMAL AND HYDROLYTIC STABILITY DATA ESTERS OF EXAMPLES XXIII-XXVII

	2,2-dimethylvalerates	
	2-ethyl-2-butyl-1,3-propanediol	2,2,5,5-tetramethyl-hexanediol
Acid No.	0.06	0.02
Thermal stability:		
Percent change 100° F. vis.	−1.7	−1.2
Acid No. change	1.46	1.37
Percent decomposition	0.50	0.49
Hydrolytic stability—		
15 minutes:		
Saponification No.	20.9	20.0
Percent saponification	7.2	7.1
30 minutes:		
Saponification No.	39.0	26.0
Percent saponification	13.4	9.3

Example XXIII.—Preparation of 2-ethyl-2-butyl-1,3-propanediol ester of 2,2-dimethylvaleric acid

The preparation of the acid employed a procedure similar to that used in Example VII, with the exception that a monobromide, instead of a dibromide, was used.

The glycol used was commercially available.

The esterification procedure was similar to that used in Example IX.

Example XXIV.—Preparation of 2,2,5,5-tetramethyl-1,6-hexanediol ester of 2,2-dimethylvaleric acid

The preparation of the acid employed a procedure similar to that used in Example VII, with the exception that a monobromide, instead of a dibromide, was used.

The 2,2,5,5-tetramethyl-1,6-hexanediol was prepared as follows:

In a 3-liter, 3-necked flask fitted with a Trubore stirrer, dropping funnel, and reflux condenser with drying tube, 36 grams (0.95 mole, metal hydrides) of lithium aluminum hydride were slurried in 600 ml. of dry tetrahydrofuran. While the slurry was rapidly stirred, 126.2 grams (0.625 mole) *a,a,a',a'*-tetramethyladipic acid dissolved in 1,150 ml. of dry tetrahydrofuran were added from the dropping funnel at a rate which maintained gentle reflux (90 minutes).

The reaction was refluxed for 30 minutes, and then 1 liter of tetrahydrofuran was distilled from the flask with stirring. The flask was cooled with an ice bath; then 300 ml. of H_2O were added, very carefully at first, followed by 150 ml. of concentrated sulfuric acid in 1 liter of water and finally by 600 ml. of ether.

In a separatory funnel, the water phase was drawn off and discarded. The ether phase was extracted with 250 ml. of 10 percent sodium bicarbonate. Acidification of the bicarbonate extract gave 31.5 grams of unreacted acid. This was immediately reduced by the procedure just described.

The ether solutions from both reductions were combined, dried with sodium sulfate and calcium chloride, and stripped of ether. The product, a tan solid, was distilled in a Koelsch flask at 0.5 mm. The yield of white, waxy material, M.P. 76–79° C., was 76.8 grams (0.441 mole, 71 percent).

No carbon-hydrogen analysis was made of this new diol itself, but the composition of its pivalate ester was determined and found to check with the theoretical value.

The ethyl ester of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid was also made and reduced to the diol. A solution of 35 grams (0.173 mole) of the crude acid, 300 ml. of absolute ethanol, and 5 ml. of concentrated sulfuric acid was refluxed for 14 hours and poured into a separatory funnel with ether and water. After extraction with 10 percent $NaHCO_3$ and drying, the ether solution was stripped of ether. Distillation through a short Vigreux column gave 28.5 grams (0.111 mole, 64 percent) of colorless liquid, B.P. 92–94° at 2 mm.

Using a 1-liter, 3-necked flask equipped with Trubore stirrer, reflux condenser, and dropping funnel, 28.5 grams (0.111 mole) of the ester were added at reflux rate to a slurry of 4.5 grams (0.119 mole, metal hydrides) of lithium aluminum hydride in 150 ml. of ether. The mixture was refluxed for 30 minutes after the addition. About 40 ml. of H_2O were added carefully to the cooled flask, followed by 22 ml. of concentrated sulfuric acid in 200

ml. of H_2O. The resulting ether solution of product was worked up just as in the acid reduction. The yield of diol (undistilled) was 17.6 grams (0.101 mole, 91 percent).

The esterification procedure was similar to that used in Example IX.

Example XXV.—Preparation of 2-methyl-2-propyl-1,3-propanediol ester of 2-methyl-2-ethylhexanoic acid

The preparation of the acid employed a procedure similar to that used in Example VII, with the exception that a monobromide, instead of a dibromide, was used.

The glycol used was commercially available.

The esterification procedure was similar to that used in Example IX.

Example XXVI.—Preparation of 2,2,5,5-tetramethyl-1,6-hexanediol ester of 2-methyl-2-ethylhexanoic acid

The preparation of the acid employed a procedure similar to that used in Example VII, with the exception that a monobromide, instead of a dibromide, was used.

The preparation of the glycol is described in Example XXIV.

The esterification procedure was similar to that used in Example IX.

Example XXVII.—Preparation of 2-methyl-2-propyl-1,3-propanediol ester of 2,2-dimethyltetradecanoic acid

The preparation of the acid employed a procedure similar to that used in Example VII, with the exception that a monobromide, instead of a dibromide, was used.

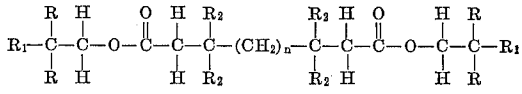
The glycol used was commercially available.

The esterification procedure was similar to that used in Example IX.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made; and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. Chemical compounds having the formula



where R is an acyclic alkyl group of from 1 to 4 carbon atoms, R_1 is an acyclic alkyl group of from 1 to 10 carbon atoms, R_2 is an acyclic alkyl group of from 1 to 4 carbon atoms and n is an integer of from 1 to 9.

2. The chemical compound di-(2,2-dimethylhexyl)-3,3,6,6-tetramethylsuberate.

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