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ESTERS OF TRIS(POLYALKYLENEOXY) ISOCYANURATES

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ABSTRACT OF THE DISCLOSURE

Triesters of tris(hydropolyoxyalkylene)isocyanurates and alkanoic or alkenoic acid are fluid over a wide temperature range. The products are useful in functional fluid and lubricating applications, such as lubricating additives to gasoline.

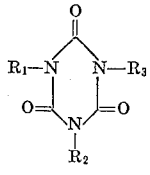
BACKGROUND OF THE INVENTION

This invention relates to novel isocyanurate derivatives, and in particular to esters of tris(hydropolyoxyalkylene)-isocyanurates.

Due to increasingly strenuous operating conditions to which they are subjected, materials employed in lubricating and functional fluid applications have had to conform to more stringent requirements with respect to viscosity index, pour point, thermal stability, etc. Additionally, it is often necessary that lubricating materials be increasingly compatible in various compositions in which they are to be employed, e.g., as lubricating additives in gasoline and other liquid hydrocarbon compositions. Isocyanurate derivatives have been utilized in such applications because of their excellent thermal stability, but these compounds have often been found to be inadequate in other respects, especially with respect to their solubility and low temperature fluidity characteristics.

SUMMARY OF THE INVENTION

The novel compounds of the instant invention are triesters of an alkanoic or alkenoic acid containing up to 18 carbon atoms and a tris(hydropolyoxyalkylene)isocyanurate of the formula

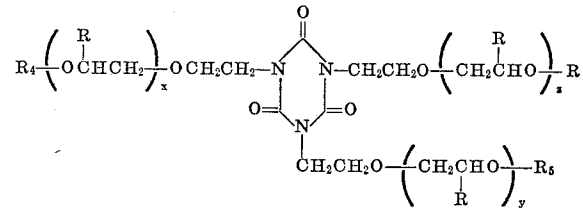


I

wherein R_1 is an hydroxyl-terminated polyalkyleneoxy chain containing from 2 to 10 oxyalkylene units, and R_2 and R_3 are each an hydroxyl-terminated oxyalkylene chain containing from 1 to 10 oxyalkylene units, each oxyalkylene unit containing from 2 to 4 carbon atoms. These materials have improved pour points and solubility characteristics, rendering them useful in lubricating and functional fluid applications, such as lubricating additives to gasoline and other liquid hydrocarbon compositions.

DETAILED DESCRIPTION OF THE INVENTION

The triesters of the instant invention are prepared from tris(2 - hydroxyalkyl)isocyanurate - alkylene oxide adducts which, in turn, are prepared by acid-catalyzed reaction of tris(2 - hydroxyalkyl)isocyanurate with alkylene oxide. Preferred triesters are those derived from ethoxylation or propoxylation of tris(2-hydroxyethyl)isocyanurate and are of the formula



II

wherein R is hydrogen or methyl; x is an integer from 1–9 and y and z are each an integer from 0 to 9; and R_4, R_5 and R_6 are each an alkanoate or alkenoate moiety containing up to 18 carbon atoms. Especially preferred are those triesters wherein x, y and z are each 1.

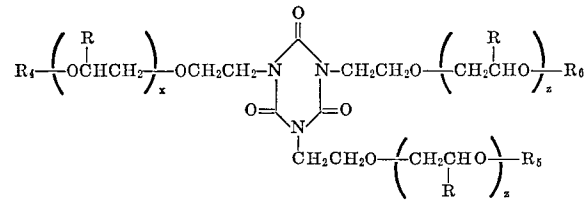
The triesters are prepared by reaction of the isocyanurate under esterification conditions with an alkanoic or alkenoic acid containing up to 18 carbon atoms, e.g., acetic, propionic, butyric, valeric, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, lauric, tridecanoic, tetradecanoic, pentadecanoic, hexadecanoic, heptadecanoic, stearic, trimethylacetic, methylpropionic, ethylhexanoic, acrylic, methacrylic, vinylacetic, γ-methylvinylacetic, γ-ethylvinylacetic, β,γ-dimethylvinylacetic, γ,γ-dimethylvinylacetic, crotonic, γ-methylcrotonic, γ-ethylcrotonic, β,γ-dimethylcrotonic, γ,γ-dimethylcrotonic, cinnamic, angelic, tiglic, undecylenic, sorbic, oleic, isooleic, petroselenic, linoleic, linolenic, eleostearic, erucic, licanic, parinaric, ricinoleic, palmitoleic and vaccenic. Any of the usual procedures employed for synthesis of esters can be employed whereby the isocyanurate is reacted with the acid or acid-generating derivative, preferably in the presence of catalyst and under conditions conducive to removal of water (or of alcohol if an ester is employed as reactant). The reactants are typically charged to a reaction vessel equipped with stirring and heating means. When the free acid is employed as reactant it is often not necessary to use additional catalyst, but when an acid-generating derivative is employed, e.g., ester or anhydride, it is usually preferred to use an acid catalyst such as sulfuric, hydrochloric, p-toluene sulfonic, ethane sulfonic, chloroacetic, boron and silicon trifluorides, monosodium sulfate, aluminum sulfate, zinc sulfate, boron trifluoride etherate, aluminum chloride, zinc chloride, aluminum alkoxides, alkyl titanates, etc. The amount of acid catalyst employed will vary with the particular reactants, catalyst and conditions, usually within the range of about 0.1–5% by weight of reactants.

The relative amounts of isocyanurate and alkanoic or alkenoic acid may vary over a broad range, but it is preferred to employ at least about 1.0 equivalent of acid per hydroxyl equivalent of isocyanurate, more preferably about 1.2 equivalents of acid. The reaction will be continued until the amount of water (or alcohol) removed indicates that the isocyanurate is approximately fully esterified.

In addition to the symmetrical triesters wherein each oxyalkylene chain of the isocyanurate is esterified with the same alkanoic or alkenoic acid, the instant invention encompasses unsymmetrical triesters, wherein the chains are esterified with different acids, and mixtures of the various esters. The unsymmetrical esters are prepared in a relatively pure manner by reacting the isocyanurate successively with one equivalent of each of the desired acids per hydroxyl equivalent. The mixtures are prepared

either by blending the individual triesters together or by reacting the isocyanurate simultaneously with a mixture of the desired acids. The latter method is preferred to obtain the mixture of unsymmetrical triesters.

Included among the novel triesters of the instant invention are the following compounds:



R	x, y, z	R_4	R_5	R_6
H	1	Acetate	Acetate	Acetate.
H	1	Propionate	Propionate	Propionate.
H	1	Butyrate	Butyrate	Butyrate.
H	1	Valerate	Valerate	Valerate.
H	1	Hexanoate	Hexanoate	Hexanoate.
H	1	2-ethyl-hexanoate.	2-ethylhexanoate	2-ethylhexanoate.
H	2	Decanoate	Decanoate	Decanoate.
H	4	Laurate	Laurate	Laurate.
CH_3	1	Stearate	Stearate	Stearate.
CH_3	1	Acrylate	Acrylate	Acrylate.
CH_3	6	Crotonate	Crotonate	Crotonate.
CH_3	6	Sorbate	Sorbate	Sorbate.
CH_3	6	Oleate	Oleate	Oleate.
CH_3	9	Hexanoate	Valerate	Butyrate.
C_2H_5	1	Octanoate	Decanoate	Laurate.
C_2H_5	1	Oleate	---do---	Oleate.
C_2H_5	1	Valerate	Heptanoate	Nonanoate.
C_2H_5	3	Vinylacetate	Trimethyl-acetate.	Trimethyl-acetate.
H	9	Cinnamate	Cinnamate	Cinnamate.
H	9	Laurate	Hexadecanoate	Stearate.
H	1	Oleate	Decanoate	Decanoate.
H	1	---do---	Oleate	Do.

Also included within the scope of the instant invention are esters of hydroxyalkylated derivatives of tris(2-hydroxypropyl)isocyanurate and tris(2-hydroxybutyl)isocyanurate, as well as derivatives wherein the oxyalkylene chains on the cyanuric acid ring are not of identical length and/or are not composed of identical oxyalkylene units. Thus, reaction of tris(2-hydroxyethyl)isocyanurate with an equimolar mixture of ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide, followed by esterification with an acid selected from among those disclosed hereinbefore, affords a product within the scoe of the instant invention.

Preferred triesters of the instant invention include the triheptanoate, tridecanoate, tripalmitate and trioleate esters of tris(hydroxypropyloxyethylisocyanurate and of tris(hydroxyethyloxyethyl)isocyanurate.

The compounds of the instant invention typically have pour points of less than 0° C., often less than −20° C., and are thermally stable at temperatures in excess of about 250° C., often in excess of 300° C.

These triesters are useful in a variety of applications due to their fluidity over a wide temperature range, thermal stability and compatibility with other materials. They are advantageously employed in lubricant applications, e.g., as mold release agents, lubricating additives in liquid hydrocarbon compositions, textile lubricants, and components of synthetic greases. They may be used for this purpose either individually or in admixture with each other or in admixture with other lubricants in a major or minor proportion. Other lubricants with which they can be used in admixture include di-2-ethylhexyl sebacate, di-isoctyl azelate, hindered esters of pentaerythritol, trimethylolethane and trimethylolpropane and alkanoic acids having a chain length of 4–12 carbon atoms, polyphenyl ethers, silicone fluids, triaryl phosphate esters, polyglycol ethers, boron esters and the like.

Additives used in connection with the instant compounds in lubricant applications include antioxidants, e.g., secondary aromatic amines such as phenothiazine, phenylnaphthylamine, diphenylamine, dialkyldiphenylamine, alkylphenothiazine, alkylphenylnaphthylamine and hindered phenolics; anti-wear/extreme pressure additives, e.g., tricresyl phosphate, chlorine or sulfur-containing phosphate esters, and chlorinated diphenyl; metal passivators, e.g., benzotriazole and derivatives thereof, other triazoles and salts of salicylol aminoguanidine as copper passivators, and quinizarin as lead passivator; and foam inhibitors, e.g., silicons.

When the instant triesters are employed as lubricating additives in liquid hydrocarbon compositions, e.g., gasoline, jet fuel, kerosene and the like, they are incorporated therein to the extent of about 0.001–5 percent by weight. When used in this manner, the instant triesters are especially advantageous in that they have detergency properties as well as lubricating.

The fluidity and thermal stability characteristics of the triesters render them valuable in functional fluid applications, especially as heat transfer agents, brake fluids and in other hydraulic fluid applications. They can be used alone for this purpose or as a component in compositions employed heretofore with which they are compatible.

The triesters are also useful as plasticizers in various resinous systems, e.g., in cellulose and vinyl resins. Compatibility in the different resins will vary with structure of the specific triester, and will depend upon the length of the oxyalkylene chains, the selection of alkanoate and/or alkenoate moiety(ies), and the specific oxyalkylene units in the chains. Once compatibility is determined by simple experimentation, the triester is incorporated in the resin of interest according to techniques which are generally familiar in the art, e.g., by blending the powdered resin with plasticizer by mixing and/or kneading to obtain uniform distribution and then curing the mix. The proportion of triester employed in this manner will vary over a great range depending upon the efficiency of the particular triester as a plasticizer, whether additional plasticizers and other modifying agents are employed, and the final degree of plasticization desired. The latter factor is dependent upon the ultimate application intended for the resin, i.e., whether it is to be fabricated into a relatively rigid or highly flexible article. With these factors in mind, one skilled in the art will utilize a "plasticizing amount" of the triesters, which amount will typically lie within the range of about 5–125, especially 35–100, parts of plasticizer per 100 parts resin.

Tris(hydropolyoxyalkylene)isocyanurates used in the preparation of the instant triesters are prepared by acid-catalyzed reaction of tris(2-hydroxyethyl)isocyanurates with alkylene oxide. The reaction may be conducted in a solvent, such as trialkylisocyanurate, N-methylpyrrolidone, acetone, etc., but is preferably conducted in the absence of solvent. In the latter method, the tris(2-hydroxyalkyl)isocyanurate is heated above its melting point and the alkylene oxide is bubbled through the molten material. An etherification-type catalyst is used in the reaction, e.g., sulfuric acid, phosphoric acid, boron trifluoride and its hydrates and etherates, trichloroacetic acid, aromatic sulfonic acids, etc. According to a typical procedure for the preparation of the tris(hydropolyoxyalkylene)isocyanurate, 75 g. of tris(2-hydroxyethyl)isocyanurate and 0.8 g. of concentrated sulfuric acid are charged into a 300 ml. stainless steel autoclave fitted with a stirrer. The charge is fused at 135° C. and liquid ethylene oxide is passed therethrough under nitrogen pressure ranging between 10 and 60 p.s.i.g. After maintaining the temperature at 134–140° C. for 2–3 hours, 77 g. of ethylene oxide are absorbed to afford a symmetrically oxyethylated isocyanurate having 3 oxyethylene units in each chain.

The following examples are provided to illustrate the instant invention more fully. They are provided for illustrative purposes only and are not to be construed as limiting the invention, which is defined by the appended claims.

EXAMPLE I

Into a reaction vessel were charged 294 g. of methyl oleate, 130 g. of tris(hydroxypropyloxyethyl)isocyanu-

rate and 2 ml. of tetraisopropyl titanate. The reaction mixture was heated to 210° C. under nitrogen until 25 ml. of methanol was removed, after which time it was heated under 1.5 mm. Hg pressure to remove unreacted methyl oleate and afford the oleic acid triester of tris(hydroxypropyloxyethyl)isocyanurate [Compound II: R=CH_3; $x=y=z=1$; $R_4=R_5=R_6$=oleate] which had pour point of −29° C. and was thermally stable beyond 300° C.

EXAMPLE II

To 384 g. of palmitic acid and 217 g. of tris(hydroxypropyloxyethyl)isocyanurate in a round bottom flask equipped with stirrer and Dean-Stark trap were added 60 ml. of toluene and 0.05 g. of p-toluenesulfonic acid. The reaction mixture was refluxed at 180° C. until 27 ml. of water were collected and then excess toluene was removed by vacuum to afford the palmitic acid triester of tris(hydroxypropyloxyethyl)isocyanurate, which was soluble in unleaded premium stock gasoline at room temperature at least to the extent of 1 weight percent.

EXAMPLE III

The procedure of Example II was repeated substituting for said palmitic acid an equivalent amount of decanoic acid to afford the decanoic acid triester of tris(hydroxypropyloxyethyl)isocyanurate, which had pour point of −25° C. and was thermally stable beyond 300° C.

EXAMPLE IV

The procedure of Example II was repeated substituting for said palmitic acid an equivalent amount of heptanoic acid to afford the heptanoic acid triester of tris(hydroxypropyloxyethyl)isocyanurate, which had pour point of −21° C. and was soluble in unleaded premium stock gasoline at room temperature at least to the extent of 1 weight percent.

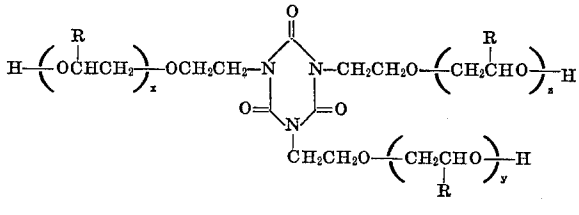
EXAMPLE V

The procedure of Example II is repeated substituting for said palmitic acid an equivalent amount of the following alkanoic and/or alkenoic acid(s) to afford the corresponding triesters of tris(hydroxypropyloxyethyl) isocyanurate:

Acetic acid
Hexanoic acid
2-ethylhexanoic acid
Hexanoic/butyric acids (equimolar mixture)
Valeric/hexanoic/heptanoic/octanoic/nonanoic acids (equimolar mixture)
Acrylic acid
Oleic/decanoic acids (equimolar mixture)
Stearic acid
Sorbic acid
Ricinoleic acid

EXAMPLE VI

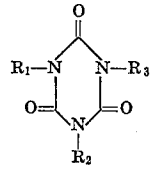
The procedure of Examples I–V are repeated substituting for said tris(hydroxypropyloxyethyl)isocyanurate an equivalent amount of the following tris(hydropolyoxyalkylene)isocyanurates to afford the corresponding triesters thereof:



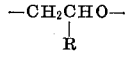
R	k	y	z
H	1	1	1
H	1	0	0
CH_3	1	0	0
H	3	3	3
H	9	9	9
C_2H_5	1	1	1
C_2H_5	2	2	2

What is claimed:

1. A compound selected from the triesters of an alkanoic or alkenoic acid containing up to 18 carbon atoms and a tris(hydropolyoxyalkylene)isocyanurate of the formula

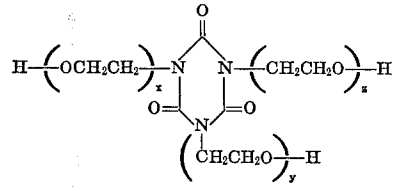


wherein R_1 is a hydrogen-terminated polyoxyalkylene chain of from 2 to 10 oxyalkylene units, and R_2 and R_3 are each a hydrogen-terminated oxyalkylene chain of from 1 to 10 oxyalkylene units, each oxyalkylene unit independently having the formula



wherein R is hydrogen, methyl or ethyl.

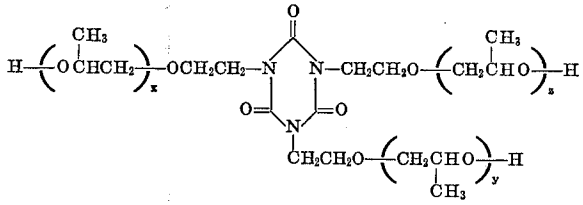
2. A compound selected from the triesters of claim 1 wherein said isocyanurate is of the formula



wherein x is an integer from 2 to 10, and y and z are each an integer from 1 to 10.

3. A compound selected from the triesters of claim 2 wherein x, y and z are each 2.

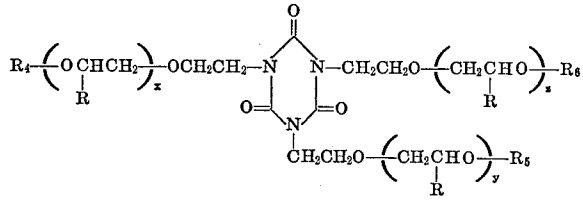
4. A compound selected from the triesters of claim 1 wherein said isocyanurate is of the formula



wherein x is an integer from 1 to 9, and y and z are each an integer from 0 to 9.

5. A compound selected from the triesters of claim 4 wherein x, y and z are each 1.

6. A compound selected from the triesters of the formula



wherein R at each occurrence is hydrogen, methyl or ethyl, R_4, R_5 and R_6 independently are selected from residues of alkanoic and alkenoic acids containing up to 18 carbon atoms, x is an integer from 1–9 and y and z are each integers from 0–9.

7. The heptanoic acid triester of tris(hydroxypropyloxyethyl)isocyanurate.

8. The decanoic acid triester of tris(hydroxypropyloxyethyl)isocyanurate.

9. The palmitic acid triester of tris(hydroxypropyloxyethyl)isocyanurate.

10. The oleic acid triester of tris(hydroxypropyloxyethyl)isocyanurate.

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JOHN M. FORD, Primary Examiner

U.S. Cl. X.R.

252—77, 51.5 R; 260—30.2