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BENZENE POLYCARBOXYLIC ACID ESTERS
Morice William Thompson, Maidenhead, England, as-
signor to Imperial Chemical Industries Limited, Lon-
don, England

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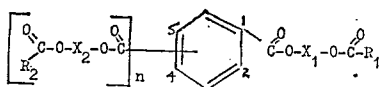
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7 Claims

ABSTRACT OF THE DISCLOSURE

New esters of structure



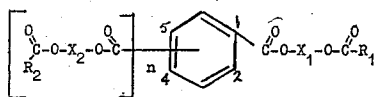
prepared by esterification of benzene polycarboxylic acids are mixed in coating compositions as plasticizers having particularly low volatility and resistance to water spotting.

FIELD OF THE INVENTION

This invention relates to esters of certain polycarboxylic acids of benzene, their preparation and their use in coating compositions.

SUMMARY OF THE INVENTION

According to the invention we provide esters of the structure:



wherein n is an integer from 1 to 3, X_1 and X_2 are straight or branched chain alkylene radicals the same or different containing from 2 to 4 carbon atoms and R_1 and R_2 are alkyl, cycloalkyl, aralkyl, aromatic or heterocyclic radicals, the same or different and containing from 1 to 18 carbon atoms in the alkyl radical.

Particularly preferred esters are those wherein the substituent in the benzene ring of variable position is in one or more of the positions numbered 2, 4, 5 with respect to the substituent of specified position in the above structural formula. The most preferred esters are those in which the substituents of the benzene ring are in the 1, 2, the 1, 2, 4, or the 1, 2, 4, 5 positions, that is they are derivatives of *o*-phthalic acid, trimellitic acid or pyromellitic acid. They may also be derivatives of the other phthalic acid isomers.

The alkylene radicals X_1 and X_2 , which may be the same or different in each substituent, may be for example ethylene, propylene, isopropylene, butylene and isobutylene.

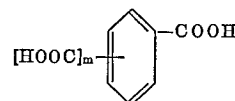
The radicals R_1 and R_2 , which may be the same or different in each substituent, may be straight or branched chain saturated or unsaturated alkyl radicals and contain up to 18 carbon atoms for example ethyl, propyl, butyl, amyl, hexyl, 2-ethyl hexyl, octyl, iso-octyl, nonyl, decyl, lauryl, tetradecyl, allyl or oleyl radicals. The preferred alkyl radicals are saturated straight or branched chain containing from 6 to 10 carbon atoms.

One or both of the radicals R_1 and R_2 may alternatively be a cyclo-alkyl radical for example cyclopentyl, cyclohexyl or cycloheptyl; or an aralkyl radical, for example benzyl, or phenyl ethyl; or an aromatic radical for example phenyl, naphthyl; or a heterocyclic radical, for exam-

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ple pyridyl. It is particularly preferred that R_1 and/or R_2 are phenyl radicals.

Although the esters may be prepared by any suitable method known in the art, they are preferably prepared by esterifying the appropriate benzene polycarboxylic acid with a hydroxy ester and according to a further feature of the invention we provide a process of preparing esters of benzene polycarboxylic acids which comprises completely esterifying a benzene polycarboxylic acid of structure:



wherein $m=1-3$, with one or more hydroxy esters formed by reacting an alkylene oxide XO wherein X is a straight or branched chain alkylene radical containing from 2 to 4 carbon atoms with a carboxylic acid



wherein R is an alkyl, cycloalkyl, aralkyl, aromatic or heterocyclic radical, the alkyl radical containing from 1 to 18 carbon atoms. Preferred benzene polycarboxylic acids are phthalic, trimellitic and pyromellitic acids and we include the use of the acid anhydrides.

Suitable alkylene oxides include ethylene oxide, 1,2-propylene oxide and 1,2-butylen oxide, and mixtures thereof but 1,2-propylene oxide is preferred.

Suitable carboxylic acids include acetic acid, butyric acid, octoic acid, lauric acid, cycloheptylic acid, benzoic acid and mixtures thereof. Particularly preferred acids are those in which R represents a straight or branched carbon chain of 6-10 carbon atoms and more particularly, 8 carbon atoms, that is octoic acid.

By way of illustrating the preparation of an ester according to the invention octoic acid may be reacted with propylene oxide to form a hydroxy ester which is then reacted with phthalic acid or the anhydride thereof to form the benzene polycarboxylic acid ester. In this case the ester produced is in fact a mixture of two isomers which may be separated only with difficulty. However, when ethylene oxide is employed an ester of unambiguous structure is obtained. The individual isomers may only be separated and characterised with great difficulty but for most applications the mixture of isomeric esters is found to be quite suitable.

We have found that the new esters and the mixtures of isomers are particularly useful as plasticisers in coating compositions and according to a further feature of this invention we provide an improved coating composition which comprises a film-forming polymer and as plasticiser a benzene polycarboxylic acid ester or mixture of esters as hereinbefore defined.

Particularly preferred compositions are those in which the film-forming polymer contains polar groups. Film-forming polymers which contain polar groups and which are commonly employed in coating compositions include homopolymers and copolymers of the lower alkyl acrylates and methacrylates, for example methyl methacrylate, homopolymers and copolymers of vinyl acetate and homopolymers and copolymers of vinyl chloride.

Film-forming polymers which are suitable in most respects for use in surface coatings, for example by virtue of their durability and ease of application, are frequently deficient in that they provide coatings which, for example, although hard may be brittle and may have poor adhesion to a substrate. It is therefore common practice to incorporate with such polymers a plasticiser which will

lessen the brittleness. However, when it is necessary to repair a damaged coating, particularly a coating based on an acrylic polymer, by a method in which the original coating is exposed to a solvent the repaired coating may suffer from "crazing." Crazing is characterised by the appearance in the coating of minute surface cracks which cause a difference in the appearance of the repaired and the un-repaired areas of the coating, and is due primarily to the loss of plasticiser from the coating either by volatilisation or by migration into an adjacent coating.

Plasticisers commonly employed in compositions which comprise a film-forming polymer are certain esters of phthalic acid, such as dibutyl phthalate and butyl benzyl phthalate, which may be used in the presence of other modifiers for the film-forming polymer. These plasticisers suffer from several disadvantages, in particular their tendency to volatilise from the coating film and to migrate into an adjacent substrate. Lacquer coatings containing these plasticisers are also liable to become marked when spots of rain water are allowed to dry upon them particularly in the sun.

We have found that when the benzene polycarboxylic acid esters of this invention, whether as the pure compounds or as a mixture of isomers, are incorporated in film-forming polymers which suffer from the disadvantages referred to above they at least equal the conventional plasticisers in reducing brittleness and improving adhesion of the film-forming polymer and also have the added advantages that they are considerably less volatile, they migrate to only a very small extent from the polymer film into adjacent substrate and there is considerably less tendency for the lacquer film to be marked by drying water droplets.

The new plasticisers may be employed in coating compositions where film-forming is present in solution and/or in dispersion. For example the composition may comprise a solution of a polymer of methyl methacrylate in a solvent such as toluene or alternatively it may comprise a fine particle-size dispersion of a polymer of methyl methacrylate in a diluent such as an aliphatic hydrocarbon. In either case the new plasticisers may be readily incorporated into the composition so that the characteristics of the final polymer film are improved. The new plasticisers are also useful in the preparation of plastisols.

Although the use of the new plasticisers is not in any way to be limited we find that they are particularly suitable in coating compositions which contain as a film-former a polymer of methyl methacrylate.

The polymer of methyl methacrylate may be a homopolymer or it may be a copolymer of methyl methacrylate with a minor proportion of other ethylenically unsaturated copolymerisable monomers, for example up to 5% of monomers such as acrylic or methacrylic acids and/or up to 25% of the lower alkyl esters of these acids, for example ethyl acrylate or butyl methacrylate. One typical film-forming methyl methacrylate polymer consists of a copolymer of 80% methyl methacrylate, 18% of ethyl acrylate and 2% of methacrylic acid.

We find that the new plasticisers have particularly good compatibility with the methyl methacrylate polymers and that there is very little migration of plasticiser from the polymer film into the undercoat over which the film is applied. When the final coating is produced by reflow of the lacquer coating on a substrate, a good gloss is obtained and there is little loss of plasticiser.

The proportion of the plasticiser to be used will depend largely on the nature of the film-forming polymer and other materials present in the coating composition and on the characteristics required in the final film. In general it is preferred to use at least 5% and not more than 60% by weight of plasticiser based on the weight of film-forming polymer.

Particularly preferred proportions of plasticiser are from 15% to 40% by weight based on the weight of film-forming polymer.

The preferred plasticisers for coating compositions are those in which in the above general formula the radicals X_1 and X_2 contain 2 or 3 carbon atoms and the radicals R_1 and R_2 are alkyl, cycloalkyl or heterocyclic radicals the alkyl radicals containing from 1 to 18 carbon atoms and particularly 6-10 carbon atoms, more particularly 8 carbon atoms, or R_1 and R_2 are phenyl or substituted phenyl radicals. It is usually preferred that the integer $n=2$, i.e. the preferred esters are those of phthalic acid.

Particularly suitable plasticisers according to the invention are phthalyl bis(β -propyl acetate), phthalyl bis(β -propyl butyrate), phthalyl bis(β -propyl nonoate), phthalyl bis(β -propyl octoate), phthalyl bis(β -propyl benzoate), phthalyl- β -propyl butyrate- β -propyl benzoate, phthalyl- β -propyl nonoate- β -propyl benzoate, pyromellityl-bis(β -propyl nonoate)-bis(β -propyl benzoate), and trimellityl-tris(β -propyl nonoate).

Coating compositions to which the plasticisers are added may contain other materials in addition to the film-forming polymer and the solvent or diluent in which the polymer is dissolved and/or dispersed. There may be present for example pigments, fillers, other conventional plasticisers, or modifiers for the main film-forming polymer or an additional film-forming polymer such as for example cellulose acetate butyrate. Solvents and/or diluents which may be present in the coating composition include ketones, alcohols, xylene, butyl acetate and aliphatic hydrocarbons.

The invention is illustrated by the following examples in which parts and percentages are by weight:

EXAMPLE 1

720 parts of n-caprylic acid and 5.27 parts of the dimethyl derivative of an amine obtained by hydrogenating the amide of coconut oil fatty acids were mixed in a pressure vessel under a nitrogen atmosphere and heated under pressure to 85° C. whilst 333.5 parts of propylene oxide were passed into the mixture. The temperature was maintained at 85 C. and the pressure maintained at 60 pounds per square inch until the acid value was less than 5 mg. KOH/gm. Excess propylene oxide was removed from the resulting crude mixture of the two stereo-isomers of β -hydroxy propyl octoate.

1,000 parts of β -hydroxy propyl octoate, 349 parts of phthalic anhydride and 135 parts of xylene were mixed with stirring, and the temperature raised to between 180° C. and 200° C. and maintained within these limits until the theoretical amount of water had been azeotroped from the mixture and the acid value was less than 10 mg. KOH/gm. The product was allowed to cool.

A sample of the product, which consisted of a mixture of stereo-isomers of phthalyl bis(β -propyl octoate), decomposed when purification by distillation under high vacuum was attempted.

EXAMPLE 2

Other benzene polycarboxylic acid esters according to the invention were prepared using a similar procedure to Example 1 but employing an aliphatic or aromatic monocarboxylic acid and a benzene polycarboxylic acid or its anhydride according to the following table:

Benzene polycarboxylic acid/acid anhydride	Aliphatic or aromatic monocarboxylic acid	Benzene polycarboxylic acid ester
Phthalic anhydride.	Acetic acid...	Phthalyl bis(β -propyl acetate).
Do.....	Butyric acid...	Phthalyl bis(β -propyl butyrate).
Do.....	Octoic acid...	Phthalyl bis(β -propyl octoate).
Do.....	Benzoic acid...	Phthalyl bis(β -propyl benzoate).
Trimellitic anhydride.	Nonoic acid...	Trimellityl tri(β -propyl nonoate).
Pyromellitic anhydride.	do.....	Pyromellityl tri(β -propyl nonoate).

5 EXAMPLE 3

An acrylic lacquer suitable for use as an automotive finish was formulated as follows:

	Parts
Polymethyl methacrylate	54.4
Cellulose acetate butyrate	20.6
Phthalyl bis(β -propyl acetate)	25.0

and pigmented with rutile titanium dioxide in a pigment:binder ratio of 0.5:1 by weight. The total solids of the pigmented lacquer was 40.0% by weight, the volatile fraction of the lacquer consisting of a mixture of solvents in the relative proportions toluene:acetone:xylof of 3.5:1:1 by weight.

The lacquer was reduced for application with a thinner containing 30 parts acetone, 40 parts toluene and 30 parts cellosolve acetate to give a viscosity of 30 seconds in a British Standard Type B No. 3 cup at 25° C. Three double coats were then applied by spray to a mild steel panel coated with a baked, high pigment volume epoxy surfacer. The panel was then baked for 15 minutes at 200° F. The film weights on the panel were 1.2 thou. of surfacer and 2.0 thou. of acrylic lacquer. The lacquer film was then sanded with 600 grade abrasive paper using white spirit as lubricant and baked for 30 minutes at 275° F.

In the following film tests a panel prepared in the manner described above but coated with a commercially available acrylic lacquer containing butyl benzyl phthalate as plasticiser was used as a control, together with the same panel prepared above:

Test	Sample	Control
Appearance.....	Smooth, high gloss....	Smooth, high gloss.
Reflow potential.....	Excellent.....	Excellent.
Chip resistance.....	do.....	Do.
Intercoat adhesion.....	do.....	Do.
Petrol resistance.....	Very good.....	Very good.
Tar and grease staining.....	Excellent.....	Excellent.
Water spotting*.....	Good resistance. No marking below 135° F.	Poor resistance. Marks at 120° F.
Volatility.....	Negligible (ratio of volatiles at 310° F= 1:10).	Significant fuming.
Cold crack cycle as described in ASTM D2246-64T	No failure.....	No failure.
60° washed gloss after 12 months exposure in Florida.	56.....	40.

*General Motors Water Spot Test in which water spots are allowed to dry slowly on the panels overnight at constant temperature, then exposed to a range of higher temperatures and that minimum temperature determined at which visible spot marks remain on the panel.

EXAMPLE 4

A lacquer suitable for use as an automotive finish was formulated as follows:

	Parts
Polymethyl methacrylate	53.2
Cellulose acetate butyrate	16.8
Phthalyl bis(β -propyl octoate)	30.0

and pigmented with rutile titanium dioxide in a pigment:binder ratio of 0.5:1 by weight. The total solids of the pigmented lacquer was 40.0% by weight and the volatile fraction of the lacquer consisted of a mixture of solvents in the relative proportions toluene:acetone:xylof or 3.5:1:1 by weight.

A test was prepared by the procedure described in Example 1 having a smooth glossy film after being reflowed

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for 30 minutes at 275° F. The film had excellent reflow potential, chip resistance, intercoat adhesion and stain resistance. The petrol resistance was very good.

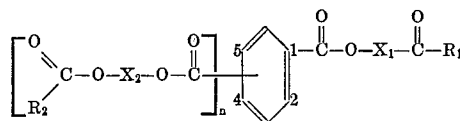
Panels prepared for the G-cycle cracking test over a nitrocellulose undercoat were subjected to the cycle described in ASTM Method D2246-64T and were free from film breakdown after 15 cycles. A conventional lacquer coating as control was cracked after the same treatment.

The volatility of the plasticiser was $\frac{1}{10}$ that of a similar lacquer in which the plasticiser was butyl benzyl phthalate.

The new ester also gave improved results when incorporated in coatings which contained polyvinyl acetate and polyvinyl chloride respectively as the film-forming materials.

We claim:

1. A coating composition which comprises a film-forming polymer selected from the group consisting of homopolymers and copolymers of lower alkyl acrylates and methacrylates, homopolymers and copolymers of vinyl acetate and homopolymers and copolymers of vinyl chloride, and 5-60%, based on the weight of said film-forming polymer, of a plasticizer having the formula



wherein n is an integer from 1 to 3, X_1 and X_2 are straight or branched chain alkylene radicals the same or different containing from 2 to 4 carbon atoms and R_1 and R_2 are each saturated straight or branched chain alkyl radicals containing from 6 to 10 carbon atoms, benzyl, phenylethyl, phenyl, naphthyl and pyridyl.

2. A coating composition according to claim 1 wherein the film-forming polymer is a homopolymer or copolymer of methyl methacrylate.

3. A coating composition according to claim 1 wherein there is present 15-40% by weight of plasticiser based on the weight of film-forming polymer.

4. A coating composition according to claim 1 wherein the substituents of the plasticizing ester are in the 1,2, the 1, 2, 4 or the 1, 2, 4, 5 positions.

5. A coating composition according to claim 1 wherein the radicals R_1 and/or R_2 of the plasticising ester are alkyl radicals containing 6 to 10 carbon atoms.

6. A coating composition according to claim 1 wherein the radicals R_1 and/or R_2 are alkyl radicals containing 8 carbon atoms.

7. A coating composition according to claim 1 wherein the radicals R_1 and/or R_2 are phenyl radicals.

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MORRIS LIEBMAN, Primary Examiner

T. MORRIS, Assistant Examiner

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