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(54) Title: POLYESTERS AND POLYESTER URETHANES

(57) Abrégé/Abstract:

The invention relates to polyesters and polyester urethanes which are stabilized against discoloration or hydrolytic degradation. At the same time, the quantity of isocyanate eliminated from polyester urethanes is considerably reduced.



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POLYESTERS AND POLYESTER URETHANES

A b s t r a c t

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POLYESTERS AND POLYESTER URETHANES

5 This invention relates to polyesters and polyester urethanes which are stabilized against discoloration or hydrolytic degradation. At the same time, the quantity of isocyanate eliminated from polyester urethanes is considerably reduced.

10 It is known that aromatic polycarbodiimides can be added to polyesters and polyester urethanes to protect them against hydrolytic degradation. Processing temperatures of up to 300°C occur in the processing of these thermoplastic or elastomeric materials, for example by injection molding and/or extrusion. The aromatic carbodiimides decompose at those temperatures and discolor the plastics in which they are present.

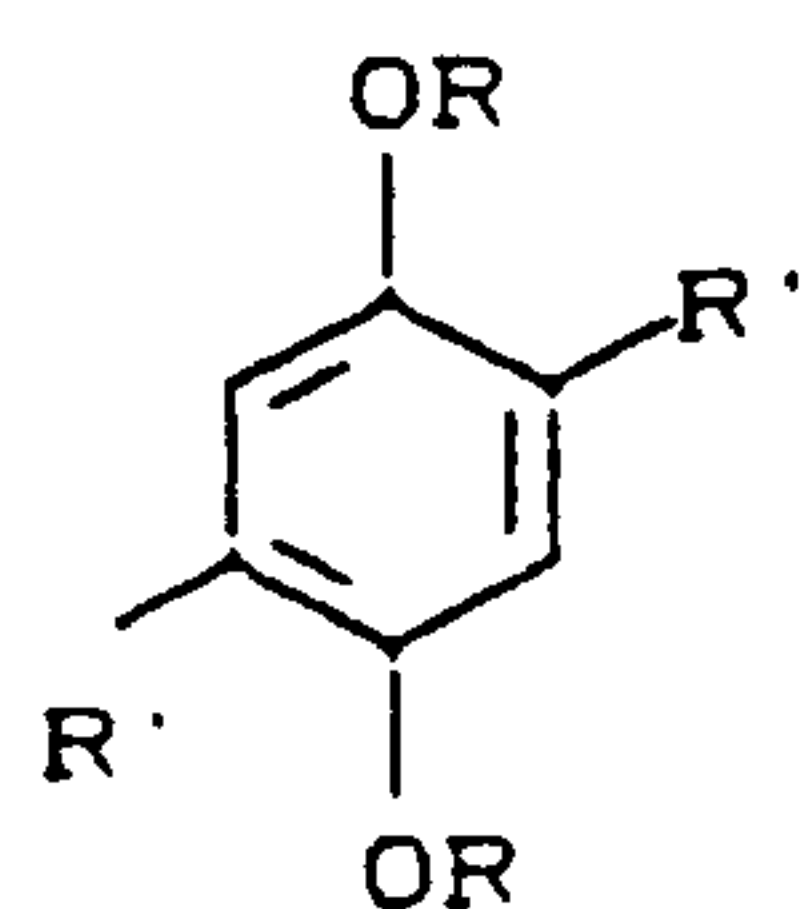
15 It has been found that this discoloration may be avoided by the addition of small quantities of benzohydroquinone or naphthohydroquinone derivatives in addition to the aromatic polycarbodiimides.

20 Accordingly, the present invention relates to polyesters and polyester urethanes stabilized against hydrolysis and discoloration which contain as stabilizers from 0.5 to 4% by weight, based on polyesters or polyester urethanes, of an aromatic carbodiimide and from 0.01 to 1.5% by weight of a benzoquinone or naphthoquinone derivative.

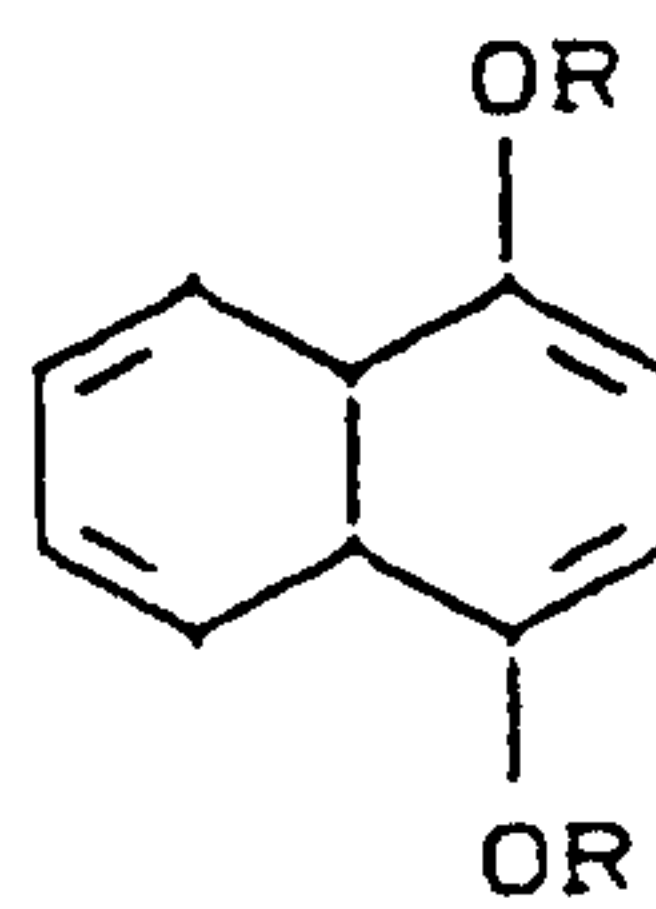
25 Polyesters in the context of the present invention are polyethylene terephthalate, polybutylene terephthalate and thermoplastic polyether ester elastomers. Polyester urethanes in the context of the present invention are urethanes which, in addition to polyether bonds, contain hydrolyzable polyester bonds, for example of adipic acid and ethylene oxide and/or propylene oxide or butane diol.

30 Aromatic polycarbodiimides in the context of the present invention are 2,2',6,6'-tetraisopropyl diphenyl

carbodiimide, homopolymeric carbodiimides of 1,3,5-triisopropyl-2,4-diisocyanatobenzene and heteropolymeric carbodiimides based on 1,3,5-triisopropyl-2,4-diisocyanatobenzene and 2,6-diisopropyl phenyl isocyanate or mixtures thereof being particularly preferred. Benzohydroquinone or naphthoquino-hydroquinone derivatives are, in particular, compounds corresponding to general formulae (I) and (II)



(I)



(II)

wherein

R represents hydrogen or C₁₋₄ alkyl and

R' represents C₁₋₄ alkyl.

Preferred benzohydroquinone and naphthohydroquinone derivatives include 2,5-di-tert. butyl 1,4-benzohydroquinone and 2-tert. butyl 1,4-benzohydroquinone.

The materials according to the present invention stabilized against hydrolysis and discoloration may be produced as follows:

The polyester having an H₂O content of ≤ 0.03%, the aromatic carbodiimide and the hydroquinone derivative are mixed together at room temperature and extruded in a twin-screw extruder at the melting temperature of the polyester. Alternatively, the materials may be separately introduced into the kneading zone of the extruder and then homogeneously distributed in the melt. After extrusion, the melt is cooled, granulated and dried. The granules obtained have an H₂O content of ≤ 0.03%.

The use of a stabilizer of the type mentioned above prevents discoloration of the polyester and considerably reduces the quantity of isocyanate eliminated from this

system by heating.

Example

5 Polyethylene terephthalate and an aromatic carbodi-
imide are mixed with one another and extruded both with and
without a stabilizer. The samples are then dried for 1 h
at 80°C. To measure the elimination of isocyanate, the
10 granules are heated in a closed container for the period of
time indicated. The quantity of isocyanate eliminated is
determined by GC against standard.

Formulations:

- 15 1. 98% polyethylene terephthalate, 2% 2,2',6,6'-tetraiso-
propyl diphenyl carbodiimide
2. 98% polyethylene terephthalate, 2% heteropolymeric
carbodiimide of 1,3,5-triisopropyl-2,4-diisocyanato-
20 benzene and 2,6-diisopropylphenyl isocyanate
3. 97.9% polyethylene terephthalate 86, 2% heteropoly-
meric carbodiimide of 1,3,5-triisopropyl-2,4-diisocya-
natobenzene and 2,6-diisopropylphenyl isocyanate, 0.1%
25 stabilizer

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Measurement A. Unground cylindrical granules, 3.5 x 3.5 mm

	1	2	3
<hr/>			
3 h/160°C			
2,6-Diisopropyl phenyl iso-)	600	55	50
cyanate)			
) ppm			
1,3,5-Triisopropyl-2,4-di-)	-	360	115
isocyanatobenzene)			
<hr/>			
4 h/150°C			
2,6-Diisopropyl phenyl iso-)	170	30	20
cyanate)			
) ppm			
1,3,5-Triisopropyl-2,4-di-)	-	200	15
isocyanatobenzene)			
<hr/>			

Measurement B. Ground granules, particle size approx. 2 mm³

	1	2	3
<hr/>			
4 h/150°C			
2,6-Diisopropyl phenyl iso-)	1300	140	90
cyanate)			
) ppm			
1,3,5-Triisopropyl-2,4-di-)	-	600	110
isocyanatobenzene)			

Example 1

97.47 g polyethylene terephthalate, 2.5 g (aromatic polycarbodiimide) and 0.03 g 2,5-di-tert. butyl (1,4-benzo-hydroquinone) are processed to a molding compound by initially mixing the carbodiimide and the benzoquinone derivative and then extruding the mixture with the polyethylene terephthalate in a twin-screw extruder at from 230 to 300°C. This material shows no discolouration, even after prolonged exposure to temperatures of from 230 to 300°C or during crystallization.

Example 2

84.7 g polyethylene terephthalate, 15.0 g (aromatic polycarbodiimide) and 0.3 g (benzoquinone derivative) are mixed as in Example 1. The compound obtained has the following properties:

Example A:

Density approx. 1.1 g/cm³
Crystallite Mp. approx. 250°C
N₂ content ≥ 0.25%

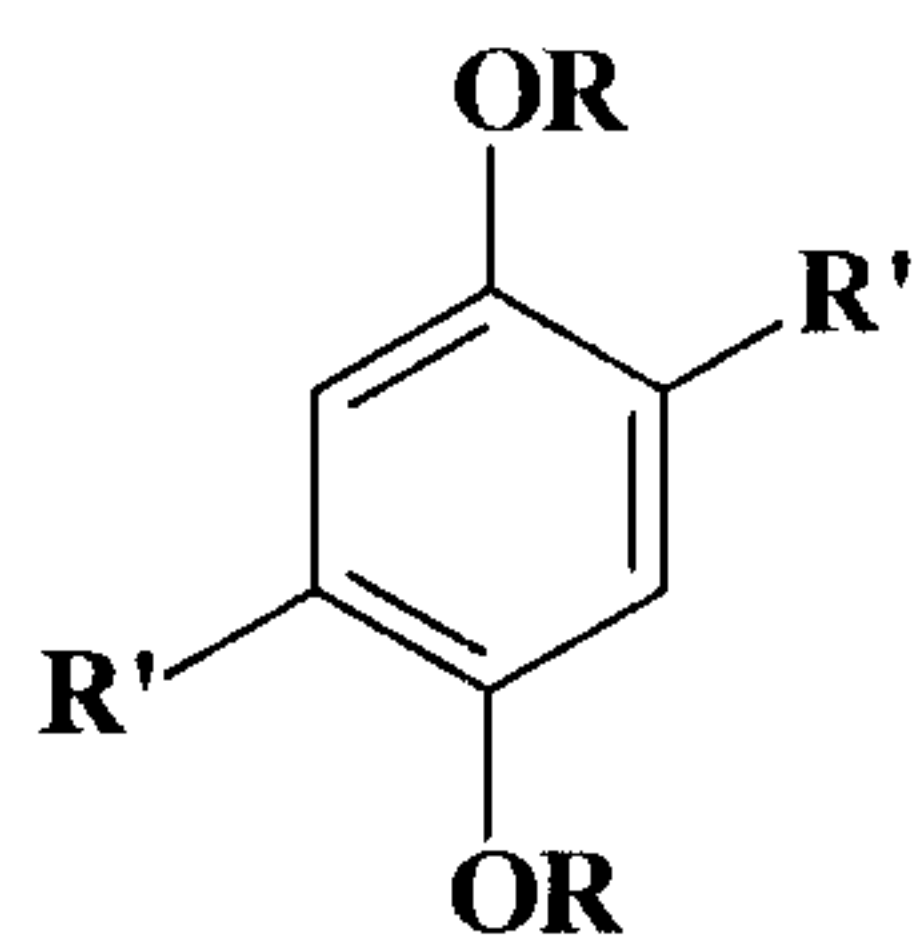
Moldings produced from this material are distinctly less discolored than a molding which has not been stabilized with an antioxidant. The following differences are determined by the CIELAB color measuring method:

DL = 9-10
DA = 2-4
DB = 4-5

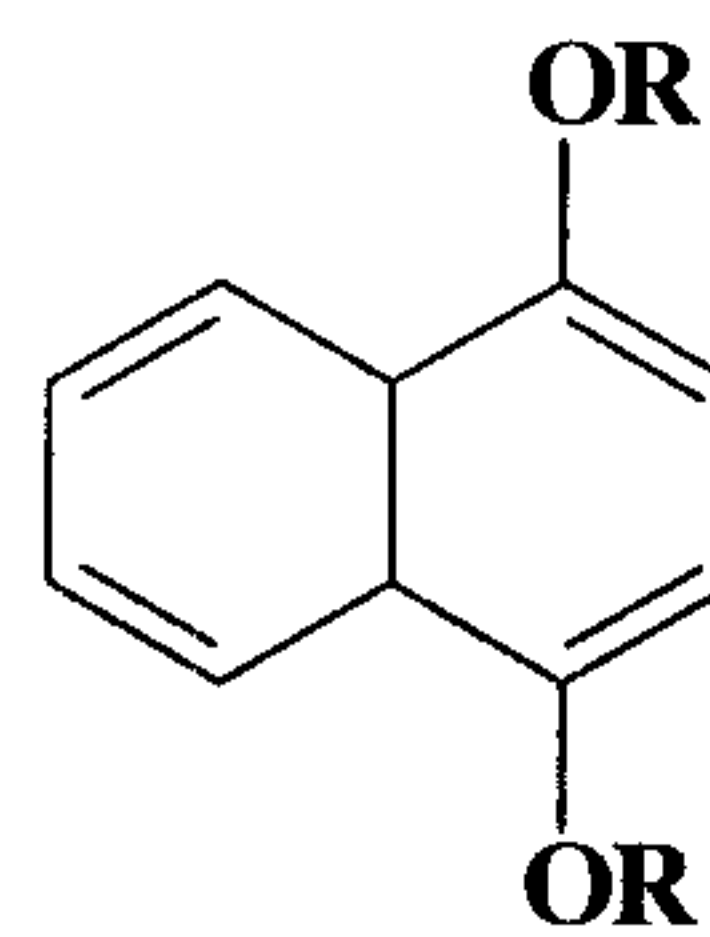
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CLAIM:

1. Polyesters or polyester urethanes or their mixtures stabilized against hydrolysis, discoloration and elimination of isocyanates, comprising from 0.5 to 4% by weight of an aromatic
 5 carbodiimide and from 0.01 to 1.5% by weight of a benzohydroquinone of Formula (I) or a naphthohydroquinone of Formula (II):



(I)



(II)

wherein

R represents hydrogen or C₁₋₄ alkyl and

R' represents C₁₋₄ alkyl.

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PATENT AGENTS