

Audio compact discs are produced by injection moulding from aromatic polycarbonates. The mouldings thus produced are metallized with aluminium by vapour deposition and are then surface-sealed with crosslinking lacquers. In addition, they are printed with dyes. Finally, they are subjected to quality control where 10% to 15% of the compact discs are rejected because of defects.

In the same way as audio compact discs, lenses are surface-sealed with crosslinking lacquers or even with polysiloxanes. In their case, too, considerable quantities of polymer waste accumulate as a result of quality control.

Lamp and headlamp reflectors are aluminium-coated. Waste accumulates both in the production of these mouldings and after their use.

Similar problems arise in the industrial application of aromatic polyester carbonates.

On account of their metal content, the lacquers or the dyes, the polycarbonate waste and/or polyester carbonate waste in question cannot be reused for other high-quality mouldings by direct re-extrusion or in the form of a blend with other polymers and/or polycondensates.

Accordingly, the problem addressed by the present invention was to work up plastic waste of the type in question by a simple, industrially workable process in such a way that the aromatic polycarbonates and the aromatic polyester carbonates could be reused.

Accordingly, the present invention relates to a process for the purification of waste of thermoplastic aromatic polycarbonates and/or thermoplastic aromatic polyester carbonates containing aluminium and/or lacquers and/or dyes, characterized in that the polycondensate waste

1. is size-reduced to fragments with a mean diameter of 0.1 cm to 5 cm and preferably 0.5 cm to 1.5 cm,

2. the fragments obtained are then stirred with dilute bases having a concentration of 0.01 mole to 2.5 moles per litre of solvent for 20 to 300 minutes and preferably for 90 to 180 minutes at temperatures of 10°C to 100°C and preferably at temperatures of 70°C to 95°C,
3. washed with dilute acids after removal of the bases and
4. subsequently washed with water until free from electrolytes,
5. the polycondensate fragments washed free from electrolytes are then washed with water while gently stirring so that all the lacquer components, aluminium or dye components separated from the polycondensate fragments, but not yet dissolved are rinsed out and,
6. the purified fragments of polycarbonate waste and/or polyester carbonate waste and/or polyester waste are filtered off and dried.

The polycondensate waste is preferably size-reduced to fragments in a shredder or in a mill (see, for example, "Ullmanns Encyklopädie der technischen Chemie", 4th Edition, 1972, Vol. 2, Verfahrenstechnik I (Grundoperationen), pages 2 to 34).

Bases in the context of the invention are, for example, dilute aqueous and/or dilute alcoholic solutions of alkali metal hydroxides and/or dilute aqueous and/or dilute alcoholic solutions of alkaline-earth metal hydroxides and/or dilute aqueous and/or dilute alcoholic solutions of ammonia and/or dilute aqueous and/or dilute alcoholic solutions of organic amines. Dilute aqueous solutions of alkali metal hydroxides are preferred, dilute aqueous

solutions of sodium and/or potassium hydroxide being particularly preferred.

5 The bases are used in concentrations of 0.01 mole per litre solvent to 2.5 mole per litre solvent and preferably in concentrations of 0.05 mole per litre solvent to 1.5 mole per litre solvent.

10 The quantity of base per kg of polycondensate fragments is 0.05 mole of base per kg of polycondensate to 2.5 mole of base per kg of polycondensate. Preferred ranges are from 0.5 mole to 1.5 mole per kg of polycondensate.

15 In the context of the invention, dilute acids for removing residual base are mineral acids such as, for example, hydrohalic acids, the halogen being chlorine, bromine or iodine, perchloric acid, phosphoric acid or sulfuric acid, although dilute solutions of organic acids in water, such as for example formic acid, acetic acid and/or propionic acid, may also be used.

The concentration of the dilute acids is between 0.01 mole per litre solvent and 0.5 mole per litre solvent.

20 The quantity of acids is between 0.5 kg of acid per 1000 kg of polycondensate and 6 kg of acid per 1000 kg of polycondensate.

25 Washing of the fragments and rinsing of the fragments in accordance with steps 4 and 5 of the process according to the invention is preferably carried out with distilled water at temperatures of 10°C to 100°C and preferably at temperatures of 20°C to 35°C. The washing time and quantity of water may readily be determined by the expert in each individual case. Electrolyte-free in the context of
30 the present invention means that the washing waters flowing off have a pH value of about 6 to 7.

Filtration of the rinsed fragments in accordance with step 6 of the process according to the invention is carried out in known filter units.

35 The fragments of polycondensate waste are dried in

conventional dryers (see, for example, "Ullmanns Encyklopädie der technischen Chemie", 4th Edition, 1972, Vol. 2, Verfahrenstechnik I (Grundoperationen), pages 699 to 721).

5 The polycarbonates, polyester carbonates and polyesters purified by the process according to the invention are free from troublesome impurities and may therefore be reprocessed in known manner to mouldings and also blended in known manner with other thermoplastics, for example with polyalkylene terephthalates, styrene/acrylonitrile polymers
10 or ABS graft polymers, to form blends.

The subject of the process according to the invention and its outcome were by no means logical because, on the one hand, the polycondensates in question are sensitive to bases and because it had not been expected that the predom-
15 inant quantity of lacquers and dyes used in the polycondensates would be removed and substantially dissolved by treatment with bases in accordance with the invention.

Lacquers which can be separated from the polymer and partly dissolved by the process according to the invention
20 are, for example, lacquers based on polyacrylonitrile, polyacrylate, polymethacrylate, polyvinyl chloride, melamine resin, epoxyisocyanate or polyurethane.

Dyes which can be separated by the purification process according to the invention are, for example, dyes
25 based on naphthoquinones, benzoquinones, anthraquinones and azo compounds and also organic pigments and inorganic pigments, such as iron oxides, chromium oxides and titanium dioxide.

Thermoplastic aromatic polycarbonates in the context
30 of the invention are polycarbonates which have been produced from diphenols and carbonate donors by any of the usual methods known from the literature (see, for example, H. Schnell "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York, 1964; US-PS 3,028,365
35 and DE-OS 38 32 396 (Le A 26 344)).

Diphenols for polycarbonates such as these may be, for example, hydroquinones, resorcinols, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulfines, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfones, bis-(hydroxyphenyl)-sulfoxides, α,α' -bis-(hydroxyphenyl)-diisopropyl benzenes, nucleus-alkylated and nucleus-halogenated compounds thereof.

Preferred diphenols are, for example, 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methyl butane, 1,1-bis-(4-hydroxyphenyl)-p-diisopropyl benzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methyl butane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropyl benzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane.

Particularly preferred diphenols are, for example, 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane.

Mixtures of the diphenols mentioned above may also be used.

The diphenols are either known from the literature or may be produced by known methods.

Aromatic polyester carbonates in the context of the invention are those which are synthesized from at least one aromatic bisphenol, at least aromatic dicarboxylic acid and carbonic acid. Suitable diphenols are those mentioned

above. Suitable aromatic dicarboxylic acids are, for example, orthophthalic acid, terephthalic acid, isophthalic acid, tert. butyl isophthalic acid, 3,3'-diphenyl ether dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, 4,4'-benzophenone dicarboxylic acid, 3,4'-benzophenone dicarboxylic acid, 4,4'-diphenyl sulfone dicarboxylic acid, 2,2-bis-(4-carboxyphenyl)-propane, trimethyl-3-phenylindane-4,5'-dicarboxylic acid.

Of the aromatic dicarboxylic acids, terephthalic acid and/or isophthalic acid are particularly preferred.

The aromatic polyester carbonates may be produced by methods known from the literature for the production of polyester carbonates, for example by processes in homogeneous solution, by melt transesterification processes and by the two-phase interfacial process.

Aromatic polycarbonates and aromatic polyester carbonates in the context of the invention are in particular those which also have weight average molecular weights $\bar{M}_w$ in the range from 10,000 to 200,000 and preferably in the range from 16,000 to 80,000, as determined in known manner by gel permeation chromatography.

The polycarbonate and polyester carbonate waste purified by the process according to the invention may again be processed in the same way as the original resins to a variety of mouldings, including films for example, in standard machines such as extruders or injection moulding machines.

The mouldings obtained may then be used in known manner in the electrical field, for optical applications in the automotive industry or as lamp covers or roof coverings.

They may be provided before or during processing with the usual additives, stabilizers, mould release agents etc. typically used for polycarbonates and polyester carbonates

and for polyesters in the usual quantities.

Examples

5 A. The compact disc waste (polycarbonate metallized with aluminium and coated with lacquer) used for the following tests were size-reduced beforehand to a particle size of 1 mm to 15 mm in a shredder. The shredded product thus obtained contained a total of 0.35% by weight of lacquer (crosslinked polyacrylonitrile and crosslinked polyvinyl chloride) and aluminium.

10 The relative solution viscosity of the shredded polycarbonate after mechanical separation of lacquers and aluminium (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C) was 1.196.

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Example 1

300 g of the shredded compact discs mentioned in A. are added with stirring to 450 g of a 5% sodium hydroxide solution which was then heated for 90 minutes to the boiling temperature so that all the aluminium and parts of the lacquer are dissolved and the remaining lacquer residues have separated from the polycarbonate and dissolved. After removal of the sodium hydroxide solution, the polycarbonate is washed with 10% acetic acid and then with softened water until neutral and the lacquer residues remaining are rinsed out. After filtration, the polycarbonate is dried at 120°C.

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The relative solution viscosity of the recyclate has not changed in relation to the value mentioned in A.

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Example 2

As Example 1, but with 5% potassium hydroxide solution instead of the 5% sodium hydroxide solution.

35 The relative solution viscosity of the recyclate has not changed in relation to the value shown in A.

Example 3

200 kg of a 5% sodium hydroxide solution are introduced into a 500 litre stirred tank with a flanged-on filter and flotation outlet. The tank is evacuated and then purged with nitrogen. The gas exchange was repeated another two times and, finally, a nitrogen blanket of 15 m³ nitrogen per hour was established. 100 kg of the polycarbonate waste mentioned in A. are added to the tank with continuous stirring, heated to 90°C with continuous stirring and kept at that temperature for 3 hours. After cooling to 30°C, the sodium hydroxide solution was drained off. The polycarbonate remaining in the tank is washed with 200 kg of 0.5% acetic acid and then with softened water until neutral, the lacquer residues which have separated from the polycarbonate being rinsed out. Finally, the polycarbonate is dried at 120°C.

The relative solution viscosity of the recyclate has not changed in relation to the value mentioned in A.

**CLAIM**

A process for the purification of waste of thermoplastic aromatic polycarbonates and/or thermoplastic aromatic polyester carbonates containing aluminium and/or lacquers and/or dyes, characterized in that the polycondensate waste

1. is size-reduced to fragments with a mean diameter of 0.1 cm to 5 cm,
2. the fragments obtained are then stirred with dilute bases having a concentration of 0.01 mole to 2.5 mole per litre of solvent for 20 to 300 minutes at temperatures of 10°C to 100°C,
3. washed with dilute acids after removal of the bases and
4. subsequently washed with water until free from electrolytes,
5. the polycondensate fragments washed free from electrolytes are then washed with water while gently stirring so that all the lacquer components, aluminium or dye components separated from the polycondensate fragments, but not yet dissolved are rinsed out and
6. the purified fragments of polycarbonate waste and/or polyester carbonate waste are filtered off and dried.