

Audio compact discs are produced from aromatic polycarbonates by the injection moulding process. The moulded articles thus produced are coated with aluminium by vapour deposition and the surface is sealed by means of cross-linking coatings. Additionally they are printed with dyes. Lastly a quality control is carried out wherein 10 per cent to 15 per cent of the compact discs produced are rejected because of defects.

10 Similarly to audio compact discs, lenses are surface-sealed by means of cross-linking coatings or by means of polysiloxanes. Here also considerable quantities of polymer scrap accrue as a result of the quality control.

15 Headlamp reflectors are aluminium-coated. Scrap is produced both in the manufacture of these moulded articles and in the use thereof.

Because of their aluminium content, the coatings and optionally the dyes, the said polycarbonate scrap and/or polyester carbonate scrap cannot be reused for other high-quality moulded parts, either by direct injection moulding or as a mixture with other polymers and/or polycondensates.

25 The object was, therefore, to work up the above-mentioned scrap by means of a simple, technically practicable process, so that the aromatic polycarbonates and/or aromatic polyester carbonates can be put to fresh use.

30 The present invention therefore provides a process for the purification of thermoplastic, aromatic polycarbonate scrap and/or thermoplastic, aromatic polyester carbonate scrap which contain metals - optionally in the form of metal salts - , coatings and optionally dyes, which is characterised in that the scrap is shredded into fragments having an average diameter of from 0.1 cm to 5.0 cm, preferably from 0.5 cm to 1.5 cm, the fragments are then heated together with acid under reflux with stirring, then

washed with water with stirring until neutral and finally
rewashed with water until all the coating constituents
separated from the polycondensate have been washed out, the
fragments are removed by filtration, dried and the residual
5 coating and dyes still adhering to the fragments are
optionally separated by air elutriation, wherein the
concentration of the acid in water is between 1% by weight
and 37% by weight, referred to the total weight of the
solution of acid and water.

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The present process is characterised particularly in that
the polycondensate scrap is shredded by means of a shredder
or in a mill, such as is described in the literature (see,
for example, Ullmanns Encyklopädie der technischen Chemie,
15 4th edition (1972), Volume 2 Verfahrenstechnik I

(Grundoperationen), pages 2 to 34), is heated with acid
under reflux with stirring, washed neutral with water under
gentle stirring in such a way that the coating constituents
which have separated from the polycondensate but not yet

20 dissolved are washed out of the polycondensate; the
polycondensate, after removal of the water by filtration,
is dried in conventional drying apparatus, which is
described, for example, in Ullmanns Encyklopädie der
technischen Chemie, 4th edition (1972), Volume 2

25 Verfahrenstechnik I (Grundoperationen), pages 699 to 721,
and then, optionally by air elutriation using apparatus
which is described, for example, in Ullmanns Encyklopädie
der technischen Chemie, 4th edition (1972), Volume 2
Verfahrenstechnik I (Grundoperationen), pages 57 to 69,

30 optionally separated from the coating residues or dye
residues still remaining. In all cases where the
polycondensate scrap by its nature contains no metals, the
latter are added prior to the acid, for instance as powder,
optionally also in the form of metal salts.

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Surprisingly, it has been found that namely through the
treatment of the polycondensate scrap with acid after the

metal has dissolved, the greater part of the coating is also separated from the polycarbonates and is even partly dissolved.

- 5 The said effect does not appear in the absence of a metal such as, for example, aluminium, because in the absence of aluminium reactive species such as nascent hydrogen and aluminium (III) salts cannot be formed "in situ".
- 10 According to DE-A-3 511 711 a process is known for the purification of polycarbonate scrap containing coatings and metals, whereby the coating layers are removed in a two-stage methanol bath with subsequent water purification, and the metal layers are removed in an etching reagent with
- 15 subsequent neutralisation and rinsing with water and the scrap thus freed from the layers is dried.

The simpler process according to the invention is not suggested by this instruction from DE-A-3 511 711, because

20 it was not to be expected that the coatings would also be separated by the treatment with acid.

Apart from aluminium, suitable metals for the purification process according to the invention are iron, zinc and tin.

25 But the action of iron, zinc and tin is weak compared with that of aluminium.

Examples of coatings which within the meaning of the present invention can be detached from the polymer and

30 partly dissolved are those based on polyacrylonitrile, polyacrylate, polymethacrylate, polyvinyl chloride, polysiloxane or melamine resin.

Suitable dyes for the purification process according to the

35 invention are, for example, those based on naphthaquinones, benzoquinones, anthraquinones and azo compounds, as well as

organic pigments and inorganic pigments such as iron oxides, chromium oxides and titanium dioxide.

Thermoplastic, aromatic polycarbonates within the meaning
5 of the invention are polycarbonates which have been prepared from diphenols and carbonate donors by the conventional methods known in the literature. (See, for example, H. Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York, 1964,
10 US Patent 3 028 365 and the German Patent DE-OS 3 832 396 (Le A 26 344)).

Examples of diphenols which can be used for the preparation of such polycarbonates are
15 hydroquinones,
resorcinols,
dihydroxydiphenyls,
bis(hydroxyphenyl)alkanes,
20 bis(hydroxyphenyl)cycloalkanes,
bis(hydroxyphenyl)sulphines,
bis(hydroxyphenyl)ethers
bis(hydroxyphenyl)ketones,
bis(hydroxyphenyl)sulphones,
25 bis(hydroxyphenyl)sulphoxides,
 α, α' -bis(hydroxyphenyl)diisopropylbenzenes,
as well as the ring-alkylated and ring-halogenated compounds thereof.

30 Preferred diphenols are, for example:

4,4'-dihydroxydiphenyl,
2,2-bis(4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methylbutane,
35 1,1-bis(4-hydroxyphenyl)-p-diisopropylbenzene,
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)sulphone,
2,4-bis(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane,
5 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene,
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-trimethylcyclohexane.

10 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,
15 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,
1,1-bis(4-hydroxyphenyl)cyclohexane and
1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Any mixtures of the above-mentioned diphenols may also have
20 been used.

The diphenols are either known in the literature or can be prepared by known methods.

25 Aromatic polyester carbonates within the meaning of the invention are those synthesised from at least one aromatic bisphenol, at least one aromatic dicarboxylic acid and carbonic acid. Suitable diphenols are those listed above. Examples of suitable dicarboxylic acids are orthophthalic
30 acid, terephthalic acid, isophthalic acid, tert.-butyl-isophthalic acid, 3,3'-diphenyletherdicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyletherdicarboxylic acid, 4,4'-benzophenonedicarboxylic acid, 3,4'-benzophenonedicarboxylic acid, 4,4'-diphenylsulphone-
35 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 preferably used.

The aromatic polyester carbonates can have been prepared by
5 methods which are known from the literature for the preparation of polyester carbonates, for example, by operating in homogeneous solution, by melt transesterification methods and by the two-phase interfacial method.

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Aromatic polycarbonates or aromatic polyester carbonates within the meaning of the present invention are those whereof the number average molecular weight M_n is between 5000 and 15000, preferably between 7000 and 13000,
15 determined by gel permeation chromatography using polystyrene as reference substance.

Acids within the meaning of the present invention are aqueous mineral acids such as, for example, haloid acids
20 wherein the halogen can be chlorine, bromine or iodine; perchloric acid, phosphoric acid or sulphuric acid. Acids within the meaning of the present invention are also organic acids such as, for example, formic acid or acetic acid.

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Metal salt/acid combinations suitable for non-metallised coated polycondensate scrap are, for instance, solutions of aluminium(III) halides in aqueous haloid acids, wherein the halogen can be chlorine, bromine or iodine, or haloid acids
30 together with aluminium powder.

Haloid acids and acetic acid are particularly preferred acids.

35 The concentrations of the acids in water is between 1% by weight to 37% by weight, preferably between 10% by weight

and 15% by weight, referred to the total weight of the solution of acids and water.

The period of heating under reflux is generally between 20
5 minutes and 180 minutes. The drying of the fragments removed by filtration is carried out at temperatures of from 100°C to 120°C. The polycondensate fragments optionally further purified by air elutriation can be reprocessed into technically usable polycarbonate moulded parts or polyester
10 moulded parts by means of the conventional injection moulding or extrusion processes.

They can moreover be processed to form usable mixtures with other plastics, preferably with acrylonitrile-butadiene-
15 styrene graft polymers (ABS) and/or with styrene-acrylonitrile copolymers (SAN).

Examples

A. The compact disc scrap (polycarbonate vapour-deposited with aluminium and covered with a coating) employed for the following experiments was previously shredded to a particle size of from 1 mm to 15 mm by means of a shredder. The shredded material thus obtained contained in total 0.35% by weight of coating (cross-linked polyacrylonitrile and cross-linked polyvinyl chloride) and aluminium.

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The relative viscosity in solution of the polycarbonate from the shredded material after mechanical separation of coatings and aluminium (reference substance) (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 above-mentioned compact disc shredded material is added with stirring to 450 g of a 10% hydrochloric acid solution and heated at boiling point for 35 minutes, so that all of the aluminium and parts of the coating are dissolved and the coating residues still remaining have become detached from the polycarbonate. After the removal of the hydrochloric acid, the polycarbonate is washed neutral with distilled water and in the course of this the coating residues remaining behind are washed out. After the polycarbonate has been filtered off, the polycondensate is dried at 120°C and the final coating residues are separated by air elutriation in a current of nitrogen.

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The relative viscosity in solution of the polycarbonate after the air elutriation is 1.194 (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C).

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Example 2

100 kg of the polycarbonate scrap described under A. is placed in a 500 l enamel kettle having a flanged filter and a flotation outlet. The kettle is evacuated and then flushed with nitrogen. The exchange of gas is repeated two more times and finally enveloped in nitrogen at 15 m³ per hour. 160 kg of 10 per cent hydrochloric acid is added to the contents of the kettle, which are heated to 90°C with stirring and maintained at this temperature for 1 hour. The material is then cooled to 30°C and the hydrochloric acid is discharged. The polycarbonate remaining in the kettle is washed free of acid using thrice demineralised water, whereby the coating residues detached from the polycarbonate are removed. The polycarbonate is finally dried at 120°C; air elutriation is dispensed with.

The relative viscosity in solution of the polycarbonate after drying is 1.193 (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C).

B. The polycarbonate scrap (polycarbonate covered with a coating) employed for the following experiments was previously shredded to a particle size of from 1 mm to 15 mm by means of a shredder. The shredded material thus obtained contained in total 0.5% by weight of coating (based on polysiloxane and melamine resin).

The relative viscosity in solution of the polycarbonate from the shredded material after mechanical separation of coatings (reference substance) (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C) was 1.279.

Air elutriation was dispensed with in the Examples 3 to 6.

Example 3

As in Example 1, but with 300 g of the polycarbonate scrap described under B. and 0.5 g of aluminium.

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A solution of the dried and purified polycarbonate (50 g of polycarbonate in 100 ml of dichloromethane) still contains 1/10 of the coating part, which a reference solution of the starting material (50 g of polycarbonate scrap in 100 ml of
10 dichloromethane) shows.

Relative viscosity in solution of the polycarbonate is 1.277 (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C) .

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Example 4

As in Example 1, but with 300 g of the polycarbonate scrap described under B., 450 g of 10% hydrochloric acid solution
20 and 1.5 g of aluminium powder.

A solution of the dried and purified polycarbonate (50 g of polycarbonate in 100 ml of dichloromethane) still contains 1/10 of the coating part, which a reference solution of the
25 starting material (50 g of polycarbonate scrap in 100 ml of dichloromethane) shows.

Relative viscosity in solution of the polycarbonate is 1.277 (0.5 g of polycarbonate in 100 ml of dichloromethane
30 at 23°C) .

Example 5

As in Example 1, but with 300 g of the polycarbonate scrap described under B., 450 g of 10% hydrochloric acid solution
5 and 7.3 g of aluminium(III) chloride.

A solution of the dried and purified polycarbonate (50 g of polycarbonate in 100 ml of dichloromethane) still contains 1/5 of the coating part, which a reference solution of the
10 starting material (50 g of polycarbonate scrap in 100 ml of dichloromethane) shows.

Relative viscosity in solution of the polycarbonate is 1.277 (0.5 g of polycarbonate in 100 ml of dichloromethane
15 at 23°C).

Example 6 (Comparison example)

As in Example 1, but with 300 g of the polycarbonate scrap described under B., 450 g of 10% hydrochloric acid solution
20 and without aluminium powder.

A solution of the dried and purified polycarbonate (50 g of polycarbonate in 100 ml of dichloromethane) still contains
25 2/3 of the coating part, which a reference solution of the starting material (50 g of polycarbonate scrap in 100 ml of dichloromethane) shows.

Example 7

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As in Example 1, but with 450 g of a 10% acetic acid solution. Relative viscosity in solution of the polycarbonate after air elutriation is 1.194 (0.5 g of polycarbonate in 100 ml of dichloromethane at 23°C).



Claims

1. Process for the purification of thermoplastic,
aromatic polycarbonate scrap and/or thermoplastic,
aromatic polyester carbonate scrap which contain
metals and coatings, characterised in that the scrap
is shredded into fragments having an average diameter
of from 0.1 cm to 5.0 cm, the fragments are then
heated together with acid under reflux with stirring,
then washed with water with stirring until neutral and
finally rewashed with water until all the coating
constituents separated from the polycondensate have
been washed out, the fragments are removed by
filtration, dried and the residual coating and dyes
still adhering to the fragments are optionally
separated by air elutriation, wherein the
concentration of the acid in water is between 1% by
weight to 37% by weight, referred to the total weight
of the solution of acid and water.
2. Process according to claim 1, characterised in that
the concentration of the acid in water is between 10%
by weight and 15% by weight.
3. Process according to claim 1, characterised in that
the metals are contained in the form of metal salts.
4. Process according to claim 1, characterised in that
the scrap still contains dyes.
5. Process according to claim 1, characterised in that
the scrap is shredded into fragments having an average
diameter of from 0.5 cm to 1.5 cm.
6. Process according to claim 1, characterised in that
the residual coating and dyes still adhering to the
fragments are separated by air elutriation.