

A process for the treatment of metal surfaces

The present invention provides a process for the passivation of metal surfaces and the use of these passivated materials in the production or processing of polycarbonates. This process enables polycarbonates to be produced with a low content of fluorescent particles.

These materials can comprise e.g. optionally heated pipes for the transport of polycarbonate melts, tube bundles or the internal surfaces of heat exchangers, reaction vessels or filtration apparatus or other melt-conveying sections of extruders and pumps. The polycarbonate produced with the aid of this process is especially suitable for high-quality injection moulded articles, particularly those in which high transparency and a low YI (yellowness index) are important, such as e.g. optical data storage media, diffusers or panes for the automotive sector in general. The polycarbonate granules or injection mouldings produced with the aid of these plant components have a low content of fluorescent particles.

The production of polycarbonate generally takes place in plant components, i.e. pipes, reaction vessels etc., made of steel or of special steel alloys. The polycarbonate is produced, transported, evaporated, isolated or further processed in this equipment.

It has now been found that metal surfaces that come into contact with polycarbonate melts can have a disadvantageous effect on product quality.

Thus, it has been found that polycarbonate produced in these plant components exhibits a certain contamination with fluorescent particles, which is disadvantageous for the quality of injection mouldings, extrudates and sheets/films produced from this material.

High residence times of polycarbonate melts in these plant components are particularly disadvantageous to the product quality and increase the intensity of fluorescence in the material. Polycarbonate melts produced by the melt

transesterification process, for example, are in contact with metal surfaces for a prolonged period. This process in particular is therefore critical in terms of the formation of fluorescent particles, which reduce the product quality.

5 Not only high residence times but also the size of the metal surface coming into contact with the polymer melt plays a serious role. Thus, for example, plant components for the filtration of polycarbonate melts can be critical for product quality since the polycarbonate is exposed to a large metal surface. The size of the metal surface is also determined by its surface quality. Thus a polished surface is
10 more advantageous than a non-polished surface.

A process for the pre-treatment of metallic plant components that come into contact with polycarbonate melts has therefore been developed. This process enables a polycarbonate to be produced with a lower content of fluorescent particles, thus
15 distinctly improving the product quality.

In addition to use in optical data storage media, this polycarbonate is also highly suitable for the production of mouldings from the automotive glazing sector, such as e.g. diffusers. This polycarbonate is particularly advantageous in those applications in
20 which a good surface quality is required.

It is known that the pre-treatment of steels has an effect on susceptibility to corrosion. Passivation methods are described e.g. by Asami *et al.* in "Surface and Interface Analysis", 2004, 36(3), 220 – 224 or by Virtanen *et al.* in "Material Science Forum"
25 1995, 185 – 188 (Passivation of Metals and Semiconductors), 965 – 974.

None of the publications cited above relates to the treatment of metals that come into contact with polycarbonate melts. The problems of corrosion are not comparable with the requirements of polycarbonate production. The solutions found were not therefore
30 obvious.

It is known that discolouration of the polycarbonate can result from ferrous surfaces in contact with a polycarbonate melt. This is described e.g. in JP 02233733. To solve this

problem, low-iron alloys, such as e.g. alloy 59, have been used in combination with polycarbonate melts. This is described e.g. in EP 1222231 B1, WO 2000064554, WO 9954381, WO 2000007684 or in JP 07171873. Apart from the fact that constructions in alloy/Hastelloy are very expensive, so that only partial areas of a plant can ever be built from these materials, none of these publications describes specific pre-treatments of the alloys by means of which the formation of fluorescent particles in polycarbonate melts can be avoided.

In EP 0 410 425 A2, injection mouldings made of polycarbonate with a low proportion of dust are described. This is achieved in that certain machine components of the injection moulding machine, such as e.g. the screw elements, consist of certain corrosion-resistant materials, such as e.g. Hastelloy. No connection with fluorescent bodies is reported and no pre-treatment method is described.

In JP 2002 12 64 25, a melt filtration plant is described consisting of a stainless steel filter for the reduction of gel particles. No connection with fluorescent bodies is reported and no pre-treatment method is described.

In EP-A 1156071, a passivation of filter media with weak acids, such as e.g. phenol, is described. As a result, an improvement in the yellowness index of the filtered material is achieved. Fluorescent particles are not described. This method is unsuitable for the reduction of fluorescent particles. In this publication a heat treatment in nitrogen is described, whereas the present invention pre-treats oxidatively.

In US 4518440, a process for the passivation of metal surfaces with mineral acids is described. These surfaces, which have a specific chromium oxide and iron oxide content after this process, are generally passivated by the method described. No effects on the formation of fluorescent particles in polycarbonate melts are described. Comparative tests in which polycarbonate melts were treated with iron oxide and/or chromium oxide show that a distinct increase in fluorescence occurs in polycarbonate melts. Taking these results into account, this passivation method is unsuitable for polycarbonate melts.

In JP-4-161210, the coating with chromium oxide of filter media used to filter polymer melts is described. This coating is achieved by a wet chemical process. The effects on the formation of fluorescent particles are not described. A reduction in gel particles is achieved by this method. In contrast, the passivation is achieved here primarily by a thermal process. The passivation according to the invention described here is clearly more effective in terms of the formation of fluorescent particles in PC melts.

In JP 2003048975, the production of polycarbonate in the melt transesterification process is described. In this process, the molten raw materials are subjected to filtration through a passivated filter. This passivation takes place with acid and/or tempering under an inert gas atmosphere. There is no mention of the formation of fluorescent particles. The method described deviates from the method disclosed here since oxidative passivation methods are used here. The filter described in JP 2003048975 is not used for the melt filtration of polycarbonate.

None of the above-mentioned publications deals with the content of fluorescent impurities in polycarbonate. The methods mentioned above do not lead to an effective reduction in fluorescent particles in polycarbonate.

Surprisingly, it has been found that a special thermal treatment of stainless steel or stainless steel alloys leads to a significant reduction in fluorescent particles in the polycarbonate matrix. Both in unpassivated stainless steel and stainless steel alloys and in those passivated by acid treatment, this method leads to a distinct reduction in fluorescent particles.

The present invention therefore provides a process for the treatment of metal surfaces that come into contact with the polymer melt during the production or processing of polymers, preferably of polycarbonate, wherein metal surfaces are thermally pre-treated in an oxidative atmosphere, such as air.

The thermal pre-treatment is generally performed at temperatures of 200 to 1200°C, depending on the type of tempering or the corresponding tempering temperature. The duration of the thermal pre-treatment is generally 1 minute to 48 hours, preferably

2 minutes to 30 hours and particularly 10 minutes to 24 hours, and depends on the type of tempering.

5 This thermal pre-treatment can take place by annealing the metal surface in a flame, by tempering in a muffle furnace by tempering with sand in a fluidized bed or by tempering in a circulating air oven.

10 When annealing the metal surfaces in a gas flame, the temperatures are generally between 600 and 1500°C, preferably between 800 and 1200°C, when tempering in a muffle furnace, between 300 and 1000°C, preferably between 600 and 900°C, and when tempering in a circulating air oven, 200 to 500°C, preferably 300 to 400°C.

15 The duration of the thermal pre-treatment at temperatures above 600°C is generally 1 minute to 1 hour, in the temperature range from 300 to 700°C usually 30 minutes to 48 hours, preferably 30 minutes to 30 hours, particularly 2 to 25 hours, and at temperatures of 300 to 500°C generally 1 to 48 hours, preferably 2 to 30 hours, particularly 4 to 25 hours.

20 The metal parts treated by annealing are flamed out in a sand bed or fluidised bed.

The metal surfaces of the filter fleece are particularly preferably tempered in a circulating air oven at 200 to 500°C, preferably 250 to 450°C, particularly 300 to 400°C, for up to 35 hours, preferably 4 to 30 hours, particularly 8 to 26 hours. A temperature of 350°C for 24 hours is especially preferred.

25 Metal parts that are suitable for the pre-treatment are metal parts that come into contact with the polymer melt. These include, for example, pipes, supply tubes, filters and tanks. Further examples are listed elsewhere in the present application. The metal parts pre-treated according to the invention should generally be used within 14, preferably 30 10, particularly preferably 8, especially 3 days after tempering.

Prior to tempering, the metal parts can be cleaned in a suitable manner, e.g. degreased, e.g. by treating with methylene chloride. By treating with mineral acid, particularly nitric acid in concentrations of 0.5 – 65 wt.%, preferably 5 – 30 wt.%, at temperatures

of 10 to 100°C, preferably at temperatures of 15 to 80°C, and with a treatment time of 10 minutes to 24 hours, preferably 30 minutes to 8 hours, or by phosphoric acid in concentrations of 0.5 to 85 wt.%, preferably 5 – 40 wt.%, at temperatures of 10 to 150°C, preferably at 15 to 80°C, with treatment times of 10 minutes to 24 hours, preferably 30 minutes to 8 hours, passivation can be achieved. However, it is essential for this to be followed by a thermal treatment step according to the present invention in order to achieve the desired effect.

The metal parts pre-treated according to the invention can be used both in the interfacial polycondensation process and in the melt transesterification process or in the processing of polymers, at points in the production plant wherever metal parts come into contact with the polymer melt. This applies in particular to plant components (sections) which produce high thermal stress, such as concentration units, pumps or heat exchangers.

The filters or filter fleeces treated according to the invention can be used for the so-called deep bed filtration of polycarbonate.

Polymers, particularly polycarbonates, distinguished by a low content of fluorescent particles can be produced in this way.

Thus, polycarbonates produced or processed using metal parts pre-treated according to the invention have a particle count of transparent fluorescent particles with a size of between 15 and 250 µm of 0.1 – 1.8 counts/g, measured after dissolving the polycarbonate in methylene chloride and filtering it through a Teflon filter with a 5 µm pore size at an excitation wavelength of 400 – 440 nm and a 25x total magnification with an illumination time of 40 ms.

A coherent fluorescent area on the Teflon filter is automatically detected here under the conditions stated above (wavelength, total magnification, illumination time) and counted as 1 count. The individual fluorescent particles found on the Teflon filter are enumerated. The total number of fluorescent particles is divided by the mass of the

polycarbonate melt weighed out in the respective batch and the particle count (fluorescent) based on 1 gram polycarbonate (counts/g) is obtained.

5 The production of the polycarbonates takes place *inter alia* by the interfacial polycondensation process. This method of polycarbonate synthesis is widely described in the literature: reference can be made, for example, to H. Schnell, Chemistry and Physics of Polycarbonates, Polymer Reviews, vol. 9, Interscience Publishers, New York 1964, pp. 33 ff., to Polymer Reviews, vol. 10, "Condensation Polymers by Interfacial and Solution Methods", Paul W. Morgan, Interscience Publishers, New York 1965, chapter VIII, p. 325, to Drs. U. Grigo, K. Kircher and P. R. Müller "Polycarbonate" in Becker/Braun, Kunststoff Handbuch, volume 3/1, Polycarbonate, Polyacetale, Polyester, Celluloseester, Carl Hanser Verlag Munich, Vienna 1992, pp. 118 – 145, and to EP-A 0 517 044.

15 According to this process, the phosgenation of a disodium salt of a bisphenol (or of a mixture of various bisphenols) present in aqueous-alkaline solution (or suspension) takes place in the presence of an inert organic solvent or solvent mixture, which forms a second phase. The resulting oligocarbonates, present mainly in the organic phase, are condensed with the aid of suitable catalysts to form high molecular weight polycarbonates dissolved in the organic phase. The organic phase is finally separated off and the polycarbonate isolated therefrom by various work-up steps.

25 Diphenols suitable for the production of the polycarbonates to be used according to the invention are e.g. hydroquinone, resorcinol, dihydroxydiphenyl, bis(hydroxyphenyl)-alkanes, bis(hydroxyphenyl)cycloalkanes, bis(hydroxyphenyl) sulfides, bis(hydroxyphenyl) ethers, bis(hydroxyphenyl) ketones, bis(hydroxyphenyl) sulfones, bis(hydroxyphenyl) sulfoxides, α,α' -bis(hydroxyphenyl) diisopropylbenzenes, and the alkylated, ring-alkylated and ring-halogenated compounds thereof.

30 Preferred diphenols are 4,4'-dihydroxydiphenyl, 2,2-bis(4-hydroxyphenyl)-1-phenylpropane, 1,1-bis(4-hydroxyphenyl)phenylethane, 2,2-bis(4-hydroxyphenyl)-propane, 2,4-bis(4-hydroxyphenyl)-2-methylbutane, 1,3-bis[2-(4-hydroxyphenyl)-2-propyl]benzene (bisphenol M), 2,2-bis(3-methyl-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)-methylbutane, 1,3-bis[2-(3,5-dimethyl-4-hydroxyphenyl)-2-propyl]benzene, 1-bis(4-hydroxyphenyl)cyclohexane and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC) and mixtures thereof.

Particularly preferred diphenols are 4,4'-dihydroxydiphenyl, 1,1-bis(4-hydroxyphenyl)phenylethane, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclohexane and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC) and mixtures thereof.

These and other suitable diphenols are described e.g. in US-A -PS 2 999 835, 3 148 172, 2 991 273, 3 271 367, 4 982 014 and 2 999 846, in German Offenlegungsschriften 1 570 703, 2 063 050, 2 036 052, 2 211 956 and 3 832 396, the French patent specification 1 561 518, in the monograph "H. Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York 1964, pp. 28 ff.; pp. 102 ff." and in "D. G. Legrand, J. T. Bendler, Handbook of Polycarbonate Science and Technology, Marcel Dekker New York 2000, pp. 72 ff."

In the case of homopolycarbonates, only one diphenol is used and in the case of copolycarbonates, several diphenols are used, it being possible, of course, for the bisphenols used, as well as all other chemicals and auxiliary substances added to the synthesis, to be contaminated with the impurities originating from their own synthesis, handling and storage, although it is desirable to work with raw materials that are as clean as possible.

The monofunctional chain terminators required to regulate the molecular weight, such as phenol or alkylphenols, particularly phenol, p-tert.-butylphenol, isooctylphenol, cumylphenol, the chlorocarbonates thereof or acid chlorides of monocarboxylic acids or mixtures of these chain terminators, are either fed into the reaction with the bisphenolate or bisphenolates or added to the synthesis at any point in time, provided that phosgene or chlorocarbonic acid terminal groups are still present in the reaction mixture or, in the case of the acid chlorides and chlorocarbonates as chain terminators,

provided that sufficient phenolic terminal groups of the forming polymer are available. Preferably, however, the chain terminator or terminators are added after the phosgenation at a location where or at a time when no more phosgene is present but the catalyst has not yet been metered in, or they are metered in before the catalyst, together
5 with the catalyst or in parallel to the catalyst.

Any branching agents or mixtures of branching agents to be used are added to the synthesis in the same way, but usually before the chain terminators. Trisphenols, quaterphenols or acid chlorides of tri- or tetracarboxylic acids, or mixtures of the
10 polyphenols or acid chlorides, are usually used.

Some of the compounds with three or more phenolic hydroxyl groups that can be used are e.g. phloroglucinol, 4,6-dimethyl-2,4,6-tris(4-hydroxyphenyl)-2-heptene, 4,6-dimethyl-2,4,6-tris(4-hydroxyphenyl)heptane, 1,3,5-tris(4-hydroxyphenyl)benzene,
15 1,1,1-tris(4-hydroxyphenyl)ethane, tris(4-hydroxyphenyl)phenylmethane, 2,2-bis[4,4-bis(4-hydroxyphenyl)cyclohexyl]propane, 2,4-bis(4-hydroxyphenylisopropyl)phenol, tetrakis(4-hydroxyphenyl)methane, 3,3-bis(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

20 Some of the other trifunctional compounds are 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

Preferred branching agents are 3,3-bis(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole and 1,1,1-tris(4-hydroxyphenyl)ethane.
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Catalysts used in the interfacial polycondensation synthesis are tert. amines, particularly triethylamine, tributylamine, trioctylamine, N-ethylpiperidine, N-methylpiperidine, N-i/n-propylpiperidine; quaternary ammonium salts such as
30 tetrabutylammonium / tributylbenzylammonium / tetraethylammonium hydroxide / chloride / bromide / hydrogen sulfate / tetrafluoroborate; as well as the phosphonium compounds corresponding to the ammonium compounds. These compounds are described in the literature as typical interfacial polycondensation catalysts, are

commercially available and are familiar to the person skilled in the art. The catalysts can be added to the synthesis individually, as a mixture, or together and successively, optionally also before the phosgenation, although additions after the introduction of phosgene are preferred unless an onium compound or mixtures of onium compounds are used as catalysts, in which case an addition before the metering in of phosgene is preferred. The metering in of the catalyst or catalysts can take place in bulk, in an inert solvent, preferably that of the polycarbonate synthesis, or also as an aqueous solution, and in the case of the tertiary amines, as their ammonium salts with acids, preferably mineral acids, particularly hydrochloric acid. When using several catalysts or when metering in partial quantities of the total quantity of catalyst, different metering methods may of course also be employed at different locations or at different times. The total quantity of the catalysts used is between 0.001 and 10 mole % based on moles of bisphenols used, preferably 0.01 to 8 mole %, particularly preferably 0.05 to 5 mole %.

The polycarbonate synthesis can be carried out continuously or batchwise. The reaction can therefore take place in stirred vessels, tubular reactors, forced circulation reactors or stirred vessel cascades or combinations thereof. Preferred media for these stirred vessels or tubular reactors and pipes etc. are e.g. V4A steel or Hastelloy C.

The polycarbonate solution is washed by repeatedly passing through settling vessels, stirred vessels, coalescers or separators, or combinations of these measures. These plant components also consist of the above-mentioned materials.

The polymer can be isolated from the solution by evaporation of the solvent by means of temperature, vacuum or a heated carrier gas. Other methods of isolation are crystallisation and precipitation. These process steps are also performed in containers made of the above-mentioned media. In a thermal work-up process, particular significance is attached to the material used because of the higher temperature. One such thermal work-up process is e.g. distilling off of the solvent by superheating and pressure release in a so-called "flash process" (cf. also "Thermische Trennverfahren", VCH Verlagsanstalt 1988, p. 114). All these processes are described in the patent literature and in text books and are familiar to the person skilled in the art.

When the solvent is removed by temperature (distillation) or the technically more effective flash process, highly concentrated polymer melts are obtained.

5 From the highly concentrated polymer melts thus obtained, the residues of the solvent can be removed either directly from the melt using evaporation extruders (BE-A 866 991, EP-A 0 411 510, US-A 4 980 105, DE-A 33 32 065), thin layer evaporators (EP-A 0 267 025), falling film evaporators or strand evaporators, or by friction compaction (EP-A 0 460 450), optionally also with the addition of an entrainer such as nitrogen or
10 carbon dioxide, or using a vacuum (EP-A 0 039 96, EP-A 0 256 003, US-A 4 423 207). Here too, an important part is played by the material used, which comes into contact with the polymer melt – these materials also consist of the above-mentioned media.

In particular, the pre-treatment of the metallic surfaces according to the invention is
15 important in apparatus and pipes at temperatures above 200°C, particularly when these parts are electrically heated or fluid- or steam-heated, especially when the wall temperatures are above 240°C, preferably above 300°C, and the contact time of the surface with the polymer melt is more than 10 seconds, or the temperature difference between incoming melt and heated surface (wall temperature of the metal part) is
20 greater than 60°C. The contact time in concentration steps in the interfacial polycondensation process is usually more than 10 seconds and as a rule less than 20 minutes, preferably less than 15 minutes. The contact time in melt processes is generally 30 minutes to 12 hours, preferably 1 hour to 6 hours.

25 The use of the surfaces pre-treated according to the invention is also positive when the polymer melt still contains residues of monomers, particularly those with OH or Cl terminal groups, and with a residual content of solvent, particularly chlorinated solvents such as chlorobenzene, dichloromethane, chloroform or carbon tetrachloride and mixtures thereof. The use of the metal surfaces treated according to the invention is
30 therefore particularly advantageous in the area of melt transport paths, thermal concentration steps and thermal mixers, i.e. heated pipes, heat exchangers, flash steps, thin layer evaporators, falling film and tube evaporators, strand evaporators, extruder parts and tanks, where these have wall contact with the PC melt.

Granules are obtained if possible by direct spinning of the melt and subsequent granulation or by using melt extruders by means of which spinning is performed in air or under liquid, usually water. If extruders are used, additives can be added to the melt upstream of this extruder, optionally using static mixers or by side extruders in the extruder.

In addition, the production of polycarbonates is also possible from diaryl carbonates and diphenols by the known polycarbonate process in the melt, the so-called melt transesterification process, which is described e.g. in WO-A 01/05866 and WO-A 01/05867. In addition, transesterification processes (acetate process and phenyl ester process) are described e.g. in US-A 34 94 885, 43 86 186, 46 61 580, 46 80 371 and 46 80 372, in EP-A 26 120, 26 121, 26 684, 28 030, 39 845, 39 845, 91 602, 97 970, 79 075, 14 68 87, 15 61 03, 23 49 13 and 24 03 01 as well as in DE-A 14 95 626 and 22 32 977.

The continuous process for the production of polycarbonates by the melt transesterification process is preferably characterised in that one or more dihydroxyaryl compounds with the diaryl carbonate, and optionally also other added reactants, using catalysts, after a pre-condensation without separating off the monohydroxyaryl compound formed, in multiple subsequent reaction evaporator stages the molecular weight is built up to the desired level at temperatures that rise stepwise and pressures that fall stepwise.

The devices, apparatus and reactors suitable for the individual reaction evaporator stages are, according to the process sequence, heat exchangers, pressure-relieving apparatus, separators, columns, evaporators, stirred vessels and reactors or other commercially available apparatus providing the necessary residence time at selected temperatures and pressures. The devices selected can be passivated using the process described here

By means of a melt filtration of the polycarbonate melt, produced by the melt transesterification process or by the interfacial polycondensation process, the melt can

be freed of impurities, such as e.g. foreign particles or cracked polycarbonate. This can involve the melt flowing through simple metal screens with mesh sizes of 10 – 100 μm . For more effective filtration, deep-bed filtration is suitable using multi-layer thin metal fabrics or sintered metals with pore sizes of 5 – 40 μm . Filters made of metal fleeces
5 with wires having diameters of 1 – 10 μm and a pore width of 5 to 40 μm , preferably 5 to 25 μm , are preferred. A melt filtration of this type is described e.g. in EP 1199325.

The following examples explain the invention but are not limiting.

Examples

Method of determining the content of fluorescent particles

5 The analysis of the content of fluorescent particles takes place by filtration of the polycarbonate sample in question (50 g) dissolved in dichloromethane (LiChrosolv; Merck: 1.06044 K33506244 430) (700 ml) through a Teflon filter membrane (Bohlender GmbH, D-97847 Grünsfeld) with a 5 µm pore diameter. The filter discs are dried *in vacuo* and protected from atmospheric dust by a cover. After filtration, the
10 filter surface is investigated (scanned) by means of an Axioplan 2 fluorescence microscope from Zeiss AG, Germany. Work is carried out with an excitation wavelength of 400 – 440 nm, an illumination time of 40 ms per scan and a 25x total magnification. The fluorescent particles are detected and the data evaluated using image processing software (KS 300 3.0 from Zeiss AG). Only particles with a
15 characteristic colour are counted, i.e. other particles, such as e.g. dust, are not taken into account (determined by the HSI colour model – see below). The colour parameters for recognising the fluorescent particles are adjusted such that they are the same as the parameters of the particles found in flow defects in optical discs. The scanning of the surface of the filter takes place automatically using a computer-controlled microscope
20 stage (Zeiss AG).

The individual fluorescent particles found on the Teflon filter are enumerated. The total number of fluorescent particles is divided by the mass of the polycarbonate melt weighed out in the respective batch and the particle count (fluorescent) based on
25 1 gram (counts/g) is obtained.

Depending on the test settings selected, very large fluorescent particles can also form. In order to take account of the size of the particles in the evaluation as well, the particle size density is given as a second value. This value is obtained as follows: the particles
30 are classified into diameter classes in 10 µm bands. The number of particles in a class is added up and multiplied by the diameter (in µm) of this class. By adding up these values over all the diameter classes and dividing by the mass of the polycarbonate melt used, the particle size density (PD) is obtained.

$$c = 1/m \times \sum_i n_i$$

5 c : particle count in counts/g; m : mass of polymer melt used; n_i : particle count in one diameter class

$$PD = 1/m \times \sum_{i=0}^n n_i \times d_i$$

10 PD : particle size density in counts* $\mu\text{m/g}$; d_i : diameter of the respective diameter class

In order to work out the effect of the metal surface, a stainless steel with a high surface area was used. In these tests, the internal metal fleece from a deep-bed filter suitable for the filtration of polymer melts was used. This was the filter fleece (i.e. the part relevant to the filtration) of a disc filter (Hydac Disc 12-63-M-44-2402107/Mat. 319418) in which only the external filter fleece was used, i.e. the septum and perforated orifice plate were removed. The metal fibres of the filter consist of pressed V4A fibres with diameters of approx. 5 – 7 μm . The pore size of the filter is approx. 5 μm .

HSI colour model

20 The particles are irradiated with light from a mercury vapour lamp and the reflected light is detected through a graded filter with a transmission range above 470 nm. The colour of the particles is determined using a digital colour camera Axiocam HRc from Zeiss incorporated in an Axioplan 2 microscope from Zeiss according to the HSI (hue, saturation, intensity) colour model. This method is described for example in “PC Digital Image Processing” by Hans-Jürgen Schlicht, Addison-Wesley, 1993. If the colour of the fluorescent particles is measured at a given illumination setting, an average hue value of about 80°, an average colour saturation of 150 digits and an average colour intensity of 190 digits is obtained. In the case of (compact disc) polycarbonate the colour of the matrix corresponds to a hue value of about 75°, an average colour saturation of 133 digits and an average colour intensity of 36 digits. The

correct colour locus of the particles and the matrix is determined by combining the hue, saturation and intensity values.

Reference example 1 (blank value / air)

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Thermal loading of polycarbonate without the effect of metal

130 g of polycarbonate granules (Makrolon® DP1-1265, Bayer MaterialScience AG) are charged into a 250 ml flask. This flask is immersed in a metal bath preheated to 350°C in air. The melt is stirred for 1 hour using a KPG stirrer (glass stirrer). The stirring rate is selected such that the melt does not rise up the stirrer. After the specified time, the polycarbonate melt is poured into an aluminium bowl.

50 g of the solidified melt thus obtained are dissolved in 700 ml dichloromethane (LiChrosolv; Merck: 1.06044) and filtered through a Teflon filter membrane (Bola filter membrane, 5 µm pore diameter; filter membrane thickness: 1 mm, Bohlender GmbH, D-97847 Grünsfeld). The evaluation of the particles retained on the filter takes place as described above using automatic detection with a fluorescence microscope. The result of the fluorescence measurement obtained is 0.68 counts/g.

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The result of the investigation is shown in Table 1.

Reference example 2 (blank value / Ar)

The procedure of reference example 1 is followed, but working under argon. The number of fluorescent particles is then evaluated. The result of the fluorescence measurement obtained is 1.03 counts / g (cf. Table 1).

Comparative example 3 (with unpassivated metal in air)

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130 g of polycarbonate granules (Makrolon® DP1-1265, Bayer MaterialScience AG), which have been dried *in vacuo* for approx. 4 hours at 120°C, are charged into a 250 ml flask. A strip of metal (metal from a disc filter: Hydac Disc 12-63-M-44-2402107/Mat.

319418, cut to 48 x 11 x 1 mm; only the external filter fleece which is effective for the filtration is used, the septum and "perforated plate" are removed; the filter strip was degreased with methylene chloride before use and then dried under high vacuum) is attached to a glass stirrer, which is provided at its lower end with a glass loop, with the aid of the eyelet and is bent round. This flask is immersed in a metal bath preheated to 350°C in air. The melt is stirred for 1 hour using a KPG stirrer to which the glass stirrer provided with the metal is attached. The stirring rate is selected such that the melt does not rise up the stirrer. After the specified time, the polycarbonate melt containing the piece of metal filter is poured into an aluminium bowl.

The result of the fluorescence measurement obtained is more than 140 counts/g (cf. Table 1).

Comparative example 4 (with unpassivated metal under Ar)

The test was performed as in example 3, but the melt was stirred under a protective gas atmosphere (argon).

The result of the fluorescence measurement obtained is 112.39 counts/g (cf. Table 1).

Example 5 (with passivated metal in air – according to the invention)

The test was performed as in example 3, but the metal strip was treated as follows: the metal was degreased with methylene chloride and dried *in vacuo*. The metal is then tempered in a circulating air oven at 350°C for 24 hours. The metal strip was used immediately after drying.

The result of the fluorescence measurement obtained is 1.45 counts/g (cf. Table 1). The result of the fluorescence measurement shows that significantly fewer fluorescent particles are formed as a result of the pre-treatment according to the invention.

Example 6 (with passivated metal under argon – according to the invention)

The metal strip was treated as described in example 5. The metal strip pre-treated in this way is then treated according to example 3 in the polymer melt under argon (instead of air) in the flask.

5 The result of the fluorescence measurement obtained is 1.59 counts/g (cf. Table 1).

The result shows that significantly fewer fluorescent particles are formed as a result of the pre-treatment according to the invention.

10 The following tests show that the pre-treatment of filter metal parts leads to a marked reduction in fluorescent particles in polycarbonate compared with the passivation of filter metal parts without pre-treatment of the metal parts according to the invention:

Comparative example 7 (passivation of the metal in citric acid)

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Before contact with the polycarbonate melt, the metal is treated with 10% citric acid at 50°C for 1 hour and then rinsed well with water and subsequently dried. The metal is not pre-treated according to the invention. The tempering of the metal in the polymer melt takes place in air as described in example 3.

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The result of the fluorescence measurement obtained is 46.33 counts/g (cf. Table 1).

This result of the fluorescence measurement shows that a passivation corresponding to the prior art is markedly inferior to the method according to the invention.

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Comparative example 8 (passivation with phenol)

Before being tempered in the polycarbonate melt, the metal is treated with phenol at 100°C for 1 hour. The metal is not pre-treated according to the invention. The tempering in the polymer melt takes place in air as described in example 5.

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The result of the fluorescence measurement obtained is 61.09 counts/g (cf. Table 1).

This result shows that a passivation corresponding to the prior art is markedly inferior to the method according to the invention.

Comparative example 9 (comparative test – passivation with HNO₃)

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Before being tempered in the polycarbonate melt, the metal fleece is treated in nitric acid (20%) at 80°C for one hour (a water jet vacuum is applied several times to degas the metal completely and to wet it with the passivation solution). After the treatment with nitric acid, the metal fleece is washed until neutral and rinsed with Millipore water
10 several more times and then dried in a high vacuum. The metal is not pre-treated according to the invention. The tempering in the polymer melt takes place in air as described in example 3.

The result of the fluorescence measurement obtained is 89.86 counts/g (cf. Table 1).

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Comparative example 10 (passivation according to JP 2001-026452)

The degreased metal fleece is pre-treated as follows before being tempered in the polycarbonate melt:

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A solution of 15 g sodium hydroxide, 3 g sodium phosphate, 2 g sodium nitrite, 2 g lead(VI) oxide and 0.1 g iron hydroxide (FeO(OH)) in 78 ml water is heated to reflux. The metal filter fleece is treated in this solution for 15 minutes. After washing with water until neutral, it is rinsed several more times with Millipore water. The metal is
25 not pre-treated according to the invention.

The tempering in the polymer melt takes place in air as described in example 3. The result of the fluorescence measurement obtained is 85.85 counts/g.

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Example 11 (comparative test – passivation according to US-A 4,518,440)

A degreased metal filter fleece is pre-treated as follows before being tempered in the polycarbonate melt:

The filter fleece is stored in a circulating air oven for 5 hours at 510°C. The metal is then treated with a passivation solution, which is prepared as follows:

5 2.5 g anhydrous oxalic acid, 1.3 g 30% hydrogen peroxide solution and 0.1 g concentrated sulfuric acid are dissolved in 100 ml demineralised water.

The filter fleece is treated in this solution at 60°C for 30 minutes, with stirring.

10 The filter fleece is then rinsed thoroughly with water and dried. The metal is not pre-treated according to the invention.

The tempering in the polymer melt takes place in air as described in example 3.

15 The result of the fluorescence measurement obtained is 3.99 counts/g. Moreover, the particles formed are distinctly larger compared with the test in which the metal fleece was pre-treated according to the invention (cf. Table 1).

Comparative example 12 (filter in static melt; unpassivated)

20 Pieces measuring 15 mm x 15 mm x 2 mm are cut from a filter pack (disc filter: Hydac Disc 12-63-M-44-2402107/Mat. 319418 with a 5 µm pore size).

25 The pieces measuring 15 mm x 15 mm x 2 mm were placed on a suction filter and a chlorobenzene/methylene chloride mixture (1:1, 200 ml) was drawn through the filter with a water jet vacuum for degreasing purposes. The piece of filter fleece is then dried for 5 min at 200°C in a drying cabinet.

30 The piece of filter fleece is then placed together with 30 g of dried (12 h, 120°C, water jet vacuum) polycarbonate granules (Bayer MaterialScience AG, Makrolon® DP1-1265) in a 50 ml one-neck flask and the atmosphere in the flask is exchanged for nitrogen (evacuated and gassed with nitrogen 3 times). The flask is then heated up to 340°C, together with its contents, in a metal bath. Subsequently, the temperature is kept at 340°C for 20 minutes, evacuation is then performed with a water jet vacuum at this

temperature and the temperature is kept at 340°C for 20 minutes with a water jet vacuum, the flask is then gassed with nitrogen and kept at 340°C for a further 50 minutes and subsequently cooled. In total, the polycarbonate melt is therefore tempered with the filter fleece at 340°C for 90 minutes.

5

The filter fleece is removed before the polycarbonate melt solidifies. The polycarbonate melt is dissolved in methylene chloride and the fluorescent portions are determined according to the method described.

10 **Comparative example 13** (static melt; filter fleece passivated with H₃PO₄)

After being degreased, the piece of filter fleece was passivated for 30 min with 85% phosphoric acid at 100°C, rinsed with water, dried and then used as described in example 12. The metal is not pre-treated according to the invention. The fluorescent portions are determined according to the method described. The result is shown in Table 2.

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Comparative example 14 (static melt; filter fleece passivated with HNO₃)

20 After being degreased, the piece of filter fleece was passivated for 30 min with 65% nitric acid at 100°C, rinsed with water, dried and then used as described in example 12. The metal is not pre-treated according to the invention.

The fluorescent portions are determined according to the method described. The result is shown in Table 2.

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Example 15 (static melt; according to the invention, burning out of an "unpassivated filter fleece")

30 The piece of filter fleece taken from a test corresponding to example 12 is burnt out in a Bunsen burner flame for 5 min, cooled and used in a similar test (as in example 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

Example 16 (static melt; according to the invention)

Burning out of a "filter fleece passivated with H_3PO_4 "

- 5 The piece of filter fleece pre-treated with phosphoric acid a test corresponding to example 13 is burnt out in a Bunsen burner flame for 5 min, cooled and used in a similar test (as in example 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

10 **Example 17** (static melt; according to the invention)

Burning out of a "filter fleece passivated with HNO_3 "

- 15 The piece of filter fleece pre-treated with nitric acid a test corresponding to example 14 is burnt out in a Bunsen burner flame for 5 min, cooled and used in a similar test (as in example 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

Example 18 (according to the invention)

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Annealing of a "non-pre-treated filter fleece"

- 25 The piece of filter fleece taken from a test corresponding to example 12 is annealed in a muffle furnace for 10 minutes at 800°C , cooled and used in a similar test (as in example 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

Example 19 (according to the invention)

- 30 Annealing of a "filter fleece passivated with H_3PO_4 "

The piece of filter fleece pre-treated with phosphoric acid a test corresponding to example 13 is annealed in a muffle furnace for 10 minutes at 800°C , cooled and used in

a similar test (as in test 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

Example 20 (according to the invention)

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Annealing of a "filter fleece passivated with HNO_3 "

10 The piece of filter fleece pre-treated with nitric acid a test corresponding to example 14 is annealed in a muffle furnace for 10 minutes at 800°C , cooled and used in a similar test (as in example 12 after the degreasing and drying). The fluorescent portions are determined according to the method described. The result is shown in Table 2.

Reference example 21 (blank value without metal)

15 This example corresponds to example 12, but no filter fleece is added to the polycarbonate melt.

Table 1: Metal filter in polycarbonate melt (stirred)

Ex.	Description	Implementation	Particle count (fluorescent)	Particle size density counts· $\mu\text{m}/\text{g}$
1	Blank value	350°C / air / no metal	0.68 counts/g	30.5
2	Blank value	350°C / argon / no metal	1.03 counts/g	44.6
3	Comparative test	350°C / air / with metal (not passivated)	> 140 counts/g	16815.2
4	Comparative test	350°C / argon / with metal (not passivated)	112.39 counts/g	12079.1
5	According to the invention	350°C / air / with metal (passivated)	1.45 counts/g	73.6
6	According to the invention	350°C / argon / with metal (passivated)	0.91 counts/g	31.5
7	Comparative test	350°C / air / with metal (passivated according to prior art) citric acid	46.33 counts/g	6086.1
8	Comparative test	350°C / air / with metal (passivated according to prior art) phenol	61.09 counts/g	6177.9
9	Comparative test	350°C / air / with metal (passivated according to prior art) HNO ₃	89.86 counts/g	10948
10	Comparative test	350°C / air / with metal (passivated according to JP 2001-026542	85.85 counts/g	12779.6
11	Comparative test	350°C / air / with metal (passivated according to US-A 4,518,440)	3.99 counts/g	477.1

The results show that the method according to the invention leads to a significantly lower formation of fluorescent fisheyes. The values resulting from the process according to the invention are no higher, or only slightly higher, compared with a tempering of polycarbonate that has not been in contact with a metal surface. This means that the method according to the invention is an effective method of avoiding the formation of fluorescent fisheyes. All other pre-treatment methods according to the prior art are clearly less effective where the formation of fluorescent particles is concerned.

Table 2 Metal filter in polycarbonate melt (not stirred)

Example	Description	Description	Particle count (fluorescent) (counts/g PC)
12	Comparative test	Unpassivated filter fleece	60.4
13	Comparative test	Filter fleece passivated with H_3PO_4	63.3
14	Comparative test	Filter fleece passivated with HNO_3	81.5
16	According to the invention	Burning out of a filter fleece passivated with H_3PO_4	0.4
17	According to the invention	Burning out of a filter fleece passivated with HNO_3	0.2
18	According to the invention	Annealing of an unpassivated filter fleece	2.2
19	According to the invention	Annealing of a filter fleece passivated with H_3PO_4	0.7
20	According to the invention	Annealing of a filter fleece passivated with HNO_3	1.2
21	Blank value	Without addition of a filter strip	0.7

The results clearly show that it is not the passivation using phosphoric or nitric acid that causes a significant reduction in fluorescent particles, but the thermal treatment using a Bunsen burner flame or muffle furnace. A metal pre-passivated with mineral

acid can, however, obtain a passivation favourable for polycarbonate by means of a further thermal treatment.

5 The different values between examples in which the polymer melt was stirred compared with those in which the polymer melt was in stationary contact with the metal are explained by the different methods (flushing of the filter).

Claims

1. A process for the treatment of metal surfaces coming into contact with the polymer melt during the production or processing of polycarbonates, characterised in that the metal surfaces are pre-treated in a first step prior to the thermal treatment with mineral acid and subsequently in a second step thermally pre-treated in an oxidative atmosphere.
2. Process according to claim 1, wherein the thermal pre-treatment is carried out at temperatures of 200 to 1200°C.
3. Process for the melt filtration of polycarbonate using a stainless steel filter, wherein the melt filter has been treated according to claims 1 to 2 prior to contact with the polymer melt.
4. Process for the production or processing of polycarbonate according to claim 3, wherein metal surfaces of, in particular, heated pipes, tanks, extruder parts have been treated at temperatures of 200 to 1200°C according to claims 1 to 2 before use.