

Process for the preparation of polycarbonates

The present invention provides a process for the continuous preparation of polycarbonates by the method of the two-phase interface process using a specific metering rate for catalysts, which renders possible the preparation of a polycarbonate with a low nitrogen content, and the polycarbonates obtainable by this process.

The two-phase interface process has proved itself for many years in the preparation of polycarbonates. The process renders possible the preparation of thermoplastic polycarbonates for a number of fields of use, such as e.g. data carriers (CD, DVD), optical or medical uses.

Polycarbonates can in principle be prepared by the two-phase interface process or the melt process.

By the two-phase interface process, they can be prepared completely continuously, as is described e.g. in EP-A 1 249 463.

In continuous process variants by the interface process it has been found in particular that the polycarbonates prepared contain a small amount of nitrogen which has been incorporated into the polycarbonate.

However, the properties of the polycarbonate, in particular the properties which are important for use in the field of data carriers, are adversely influenced by this incorporated nitrogen.

Polycarbonates prepared by a discontinuous process are conventionally free from nitrogen, but continuous variants are frequently desired for cost reasons.

5 Polycarbonates prepared by the melt process are conventionally also free from nitrogen, but these materials have other disadvantages, such as e.g. a high content of monomers, monocarbonates, oligomers and branched structures.

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(There was therefore the object of providing a completely continuous two-phase interface process in which the content of incorporated, bonded nitrogen is reduced to contents of between 20 and 3 ppm.

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DE-A 42 27 372 and EP-A 1 249 463 of the Applicant, in which the apparatus arrangement of the process according to the invention is already described, are to be regarded as the closest prior art. However, no doctrine at all or only
20 an indication that the nitrogen content is critical or of how this would be counteracted is to be found in the prior art.

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(It has now been found, surprisingly, that polycarbonate is obtained continuously in a very good product quality - measured by the content of incorporated nitrogen - if the metered amount of catalyst is not allowed to fall below a minimum amount of 0.012 to 0.05 mol of catalyst per mol of bisphenol employed.

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Particularly good results are achieved if this catalyst metering is used in combination with the reactor arrangement of "circulating pump reactor" - comprising a

heat exchanger with a circulating pump loop and detention tank - plus detention tubes.

5 This is particularly surprising since to reduce the nitrogen content the expert would attempt to decrease the amount of the nitrogen source, namely the catalyst. A maximum and not a minimum value would therefore be expected as the limit value.

10 The present application provides a process for the continuous preparation of polycarbonates which contain small amounts of bonded nitrogen by the method of the continuous two-phase interface process from diphenols, phosgene, chain terminators, catalyst and optionally
15 branching agents in a mixture of aqueous-alkaline phase and organic solvent phase, characterized in that the metered amount of catalyst is not allowed to fall below a minimum amount of 0.012 to 0.05 mol of catalyst per mol of bisphenol employed.

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(This process preferably comprises the following process steps:

- 25 1. Continuous bringing together of the organic phase and the aqueous phase in the circulating pump loop of a circulating pump reactor, during which an emulsion forms, optionally using a mixer, wherein the organic phase is a solvent which is suitable for the
30 polycarbonate and already contains the phosgene and the aqueous phase comprises water and a mixture of alkali metal hydroxide solution and phenolic

components (bisphenol and optionally monophenol as a chain terminator),

wherein

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2. a temperature of less than 60°C, preferably 55°C - 25°C is established in the circulating pump reactor, the circulating pump reactor provides an average dwell time of at least 2 minutes, preferably between 2 and 15 minutes, and a part amount of the emulsion formed is removed continuously from the circulating pump reactor via the detention tank,
- 10

and

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3. the part amount of this emulsion removed is then pumped through tube reactors which are equipped with mixing and detention zones and provide a total dwell time of between 2 minutes and 40 minutes, preferably 2-30 minutes,
- 20

wherein

- 1) the ratio (expressed in moles/mole) of metered amount of phosgene to the amount of phosgene theoretically necessary to react all the bisphenol and phenol is between 1.12 and 1.22, preferably between 1.13 and 1.20,
- 25
- 2) phosgene solution and bisphenol solution are metered here within the circulating pump reactor directly after the detention tank, before the pump, into the circulating pump loop, optionally via a mixer, and the chain terminator can also be
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conveyed into this circulating pump loop or optionally directly into the tube reactors, see 5),

5 3) within the circulating pump reactor alkali metal hydroxide solution is topped up on the suction side of the pump in an amount of 15 - 40%, preferably 20 - 35% of the total amount to be topped up,

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(4) within the circulating pump reactor bisphenol A and phosgene solutions are metered into the circulating pump loop according to 2) such that the part amount removed at the detention tank
15 corresponds to the total amount of solutions metered in,

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5) further alkali metal hydroxide solution (85 - 60%, preferably 80 - 65% of the total alkali metal hydroxide solution to be topped up) and optionally chain terminator are added into the part amount removed from the detention tank,
(directly before introduction into the tube reactor, and

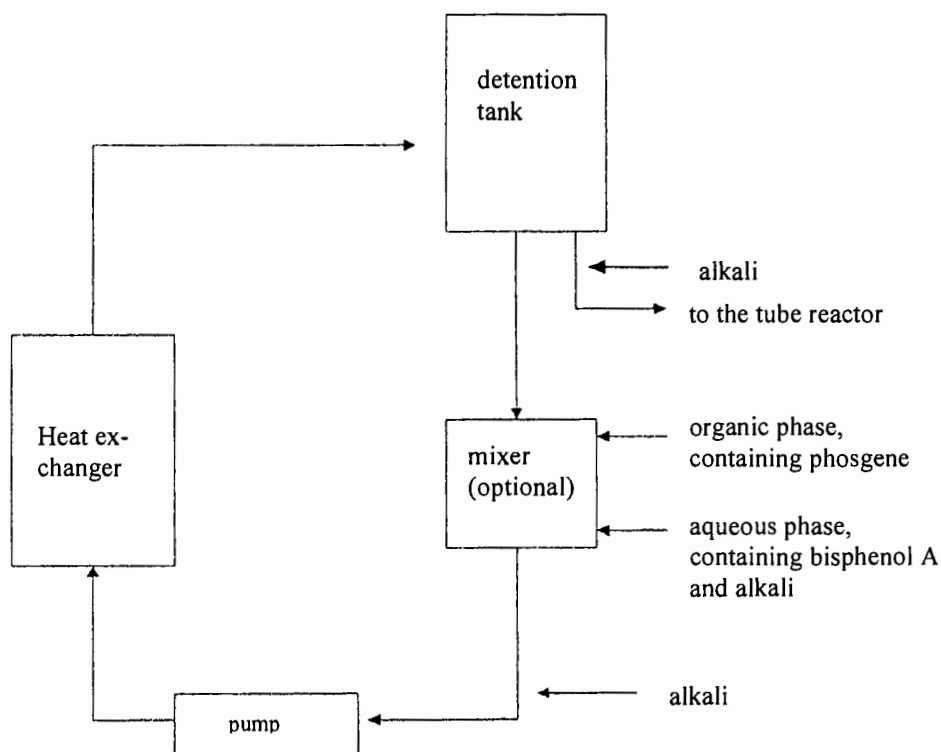
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6) after a further 1 - 20 minutes, preferably 1 - 15 minutes dwell time in the tube reactor, the catalyst is added in a ratio of at least 0.012, preferably 0.012 to 0.05, particularly preferably
30 0.012 to 0.04 and very particularly preferably 0.012 to 0.03 mol of catalyst per mol of bisphenol employed.

"after" and "before" in the present connection are always to be understood in the flow direction of the emulsion within the circulating pump reactor.

5 A circulating pump reactor comprises here a circulating pump loop, a pump for pumping the reaction emulsion in circulation, metering points, optionally designed as mixers, for the organic phase (solvent containing phosgene) and aqueous phase (alkali metal hydroxide solution and
10 diphenol component), a heat exchanger and a detention tank, which is equipped in parallel with a removal possibility for continuous removal of a part stream.

For better understanding, the "circulating pump reactor" is
15 also shown in diagram form:



A tube reactor here consists of mixing and detention tubes and is connected downstream after the removal point of the detention tank of the circulating pump reactor.

5 A preferred embodiment of the process according to the invention is obtained by adhering to the metering rates and circulating pump conditions described in EP-A 1 249 463, p. 4, 1. 1-25.

10 Surprisingly, a polycarbonate with a nitrogen content of 3 to 20 ppm is obtained by employing the process according to the invention.

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15 Suitable diphenols are those of the formula HO-Z-OH, in which Z is an aromatic radical having 6 to 45 C atoms, which can contain one or more aromatic nuclei, can be substituted and can contain aliphatic radicals or cycloaliphatic radicals or heteroatoms as bridge members.

Examples are

20 dihydroxydiphenyls,
bis-(hydroxyphenyl)-alkanes
(
bis-(hydroxyphenyl)-cycloalkanes
bis-(hydroxyphenyl) sulfides
25 bis-(hydroxyphenyl) ethers

and nucleus-alkylated and nucleus-halogenated compounds thereof.

30 These and further suitable other diphenols are described e.g. in US-PS 3 028 365, 4 982 014, 2 999 835, 3 148 172, 3 275 601, 2 991 273, 3 271 367, 3 062 781, 2 970 131 and 2 999 846, in DE-A 15 70 703, 20 63 050, 20 63 052 and 22 11

956, French Patent Specification 1 561 518 and in DE-A 38 33 953.

Preferred diphenols are:

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2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A) and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl-cyclohexane (TMC-bisphenol).

It is to be emphasized here that the process according to the invention can be employed practically for all known diphenols.

The diphenols are employed in the process according to the invention in aqueous-alkaline solution, the concentration of diphenols here being 10-20%, preferably 12.5 to 17.5%, and the amount of alkali 1.0 to 3.0 mol of alkali metal hydroxide solution per mol of bisphenol, depending on the solubility of the bisphenol employed.

The phosgene is employed in organic solvents in a concentration of 7-10%, preferably 8-9.5%.

Suitable chain terminators and branching agents are known from the literature. Some are described, for example, in DE-A 38 33 953. Preferred chain terminators are phenol, cumylphenol, isooctylphenol and para-tert-butylphenol. The chain terminators can be metered in the pure form or in various concentrations as a solution in organic solvents.

Preferred branching agents are trisphenols and tetraphenols, as well as 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole. The branching

agents can also be metered in the pure form or in various concentrations as a solution in organic solvents.

Sodium hydroxide solution or potassium hydroxide solution
5 are employed as the alkali metal hydroxide solution, and
alkaline earth metal hydroxide solutions can optionally
also be employed. Aqueous sodium hydroxide solution is
preferred. The concentration of the NaOH in the aqueous
sodium hydroxide solution corresponds to that of the
10 commercially obtainable alkalis, that is to say is between
20 and 60%, preferably between 30 and 50%, and sodium
hydroxide solution which is obtained directly from the
amalgam or membrane process, ideally the membrane process
of chlor-alkali electrolysis with concentrations of 50 or
15 32% respectively, is very particularly preferred.

All the percentage data in the present context are to be
understood as wt.%, unless explicitly stated otherwise.

20 Possible catalysts are in principle all the catalysts known
for the preparation of polycarbonates by the two-phase
interface process, such as e.g. tertiary amines. N-Ethyl-
piperidine and triethylamine are preferred.

25 The organic phase contains solvent or a solvent mixture
which dissolves polycarbonate. Suitable solvents are all
the known solvents which are capable of dissolving
polycarbonate to the extent of at least 5 wt.% at
temperatures of about 20°C, and mixtures thereof.

30 Methylene chloride, toluene and monochlorobenzene are
preferred, and methylene chloride and mixtures of methylene

chloride and monochlorobenzene in a ratio of 20:80 parts by wt. to 75:25 parts by wt. are particularly preferred.

5 A pH of between 9 and 14, preferably between 9.5 and 13.0, is established over the entire reaction. This is effected by employing the necessary amount of alkali metal hydroxide solution to dissolve the diphenols once at the start, and moreover carrying out a first topping up of the alkali metal hydroxide solution before the heat exchanger, and
10 then carrying out a second topping up of the alkali metal hydroxide solution, optionally together with the chain terminator, before the tube reactors.

The polycarbonates can be processed to any desired shaped
15 articles in a known manner, it being possible to add the conventional additives for thermoplastic polycarbonates, such as stabilizers, mould release agents or flameproofing agents, fillers or glass fibres, before or during the processing.

20 The polycarbonates obtainable by the process according to the invention can be employed industrially in a known manner as any desired shaped articles or also as sheets and films, for example in the automobile sector or in optical
25 uses, in particular also in optical and magneto-optical storage media.

The following uses may be mentioned by way of example but without being limiting:

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1. Safety panes, which as is known are necessary in many areas of buildings, vehicles and aircraft, and as shields of helmets.

2. Production of foils, in particular ski foils.
3. Production of blow mouldings (see, for example, US
5 Patent 2 964 794), for example 1 to 5 gallon water
bottles.
4. Production of light-transmitting sheets, in particular
10 hollow chamber sheets, for example for covering
(buildings such as railway stations, greenhouses and
lighting installations.
5. Production of optical data stores.
- 15 6. For production of traffic light housings or traffic
signs.
7. For production of foams (see, for example, DE-B 1 031
507).
- 20 8. For production of threads and wires (see, for example,
(DE-B 1 137 167 and DE-A 1 785 137).
9. As translucent plastics with a content of glass fibres
25 for lighting purposes (see, for example, DE-A 1 554
020).
10. As translucent plastics with a content of barium
30 sulfate, titanium dioxide and/or zirconium oxide or
organic polymeric acrylate rubbers (EP-A 634 445, EP-A
269 324) for the production of light-transmitting and
light-scattering mouldings.

11. For production of precision injection mouldings, such as, for example, lens holders. Polycarbonates with a content of glass fibres which optionally additionally contain about 1 - 10 wt.% MoS₂, based on the total weight, are used for this.
12. For production of optical apparatus components, in particular lenses for photographic and film cameras (see, for example, DE-A 2 701 173).
13. As light transmission carriers, in particular as light conductor cables (see, for example, EP-A1 0 089 801).
14. As electrical insulating materials for electrical conductors and for plug housings and plug connectors.
15. Production of mobile telephone housings with improved resistance to perfume, shaving lotion and skin perspiration.
16. Network interface devices.
17. As a carrier material for organic photoconductors.
18. For production of lamps, e.g. searchlight lamps, as so-called "headlamps", diffuser panes or internal lenses.
19. For medical uses, e.g. oxygenators, dialysers.
20. For foodstuffs uses, such as e.g. bottles, utensils and chocolate moulds.

21. For uses in the automobile sector where contact with fuels and lubricants may occur, such as, for example, bumpers, optionally in the form of suitable blends with ABS or suitable rubbers.
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22. For sports articles, such as e.g. slalom poles or ski shoe buckles.
23. For household articles, such as e.g. kitchen sinks and letter-box housings.
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24. For housings, such as e.g. electrical distribution cabinets.
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25. Housings for electric toothbrushes and hairdryer housings.
26. Transparent washing machine portholes with improved resistance to the wash solution.
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27. Safety glasses, optical correction glasses.
28. Lamp covers for kitchen equipment with improved resistance to kitchen vapour, in particular oil vapours.
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29. Packaging films for medicaments.
30. Chip boxes and chip carriers.
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31. For other uses, such as e.g. feed stable doors or animal cages.

The following examples are intended to illustrate the present invention, but without limiting it.

Examples**Example 1**

5 Via a T-piece, before the pump, 24,000 kg/h of an alkaline
bisphenol A solution which contains 15 wt.% BPA and 2.1 mol
of sodium hydroxide solution per mol of BPA and, via a
further T-piece, 1,840 kg/h of phosgene dissolved in 21,000
10 kg/h of solvent, which consists of 50 wt.% methylene
chloride and 50 wt.% monochlorobenzene, are metered into a
circulating pump reactor.

To maintain the alkalinity, 348 kg/h of 32% sodium
hydroxide solution are metered in and the reaction mixture
15 is passed back to the pump via the heat exchanger and the
detention tank, the above substance streams being metered
in.

The temperature is 38°C.

20 A part amount of the emulsion which is as high as that of
the raw materials flowing in is fed before the metering
points for BPA and phosgene from the detention tank to a
further pump and pumped through a tube reactor. 1,064 kg/h
25 of sodium hydroxide solution (32 wt.%) and 703 kg/h of a
solution (20 wt.%) of p-tert-butylphenol, dissolved in the
solvent mixture (50 parts methylene chloride and 50 parts
monochlorobenzene), are metered into this stream. After a
dwell time of 10 min, 29 kg/h of N-ethylpiperidine (0.0163
30 mol per mol of bisphenol A) in the form of a 5.2% solution
in the solvent mixture (50 parts methylene chloride and 50
parts monochlorobenzene) are metered in and the emulsion is

pumped through a further tube reactor by means of a further pump.

5 After a dwell time of a further 10 min, the emulsion is separated in a separating vessel and the polycarbonate solution is washed free from electrolytes by known processes, e.g. by the centrifuge technique.

10 The polycarbonate solution is concentrated in evaporation units and freed from residual solvent on a devolatilization extruder.

The following analytical data are determined on the polycarbonate granules:

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YI = 1.33*

Eta rel = 1.196**

Phenol. OH = 90 ppm***

Nitrogen = 8 ppm****

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* measured in accordance with ASTM E 313

** measured in accordance with ISO 1628/4

*** measured by UV spectroscopy at 546 nm after a colour reaction of the phenol. end groups with TiCl_4

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**** measured in accordance with ASTM D 4629 and DIN 51444 (determination of nitrogen by the Antek method).

Example 2

30 Via a T-piece, before the pump, 27,000 kg/h of an alkaline bisphenol A solution which contains 15 wt.% BPA and 2.1 mol of sodium hydroxide solution per mol of BPA and, via a further T-piece, 2,090 kg/h of phosgene dissolved in 22,950

kg/h of solvent, which consists of 50 wt.% methylene chloride and 50 wt.% monochlorobenzene, are metered into a circulating pump reactor.

5 To maintain the alkalinity, 445 kg/h of 32% sodium hydroxide solution are metered in and the reaction mixture is passed back to the pump via the heat exchanger and the detention tank, the above substance streams being metered in.

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(The temperature is 38°C.

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A part amount of the emulsion which is as high as that of the raw materials flowing in is fed before the metering points for BPA and phosgene from the detention tank to a further pump and pumped through a tube reactor. 1,135 kg/h of sodium hydroxide solution (32 wt.%) and 740 kg/h of a solution (20 wt.%) of p-tert-butylphenol, dissolved in the solvent mixture (50 parts methylene chloride and 50 parts monochlorobenzene), are metered into this stream. After a dwell time of 9 min, 36 kg/h of N-ethylpiperidine (0.0179 mol per mol of bisphenol A) in the form of a 6.1% solution in the solvent mixture (50 parts methylene chloride and 50 parts monochlorobenzene) are metered in and the emulsion is pumped through a further tube reactor by means of a further pump.

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After a dwell time of 9 min, the emulsion is separated in a separating vessel and the polycarbonate solution is washed free from electrolytes by known processes, e.g. by the centrifuge technique.

The polycarbonate solution is concentrated in evaporation units and freed from residual solvent on a devolatilization extruder.

- 5 The following analytical data are determined on the polycarbonate granules:

YI = 1.32

Eta rel = 1.193

10 Phenol. OH = 70 ppm

Nitrogen = 5 ppm

Example 3

- 15 Via a T-piece, before the pump, 35,000 kg/h of an alkaline bisphenol A solution which contains 15 wt.% BPA and 2.1 mol of sodium hydroxide solution per mol of BPA and, via a further T-piece, 2,700 kg/h of phosgene dissolved in 31,500 kg/h of solvent, which consists of 50 wt.% methylene
20 chloride and 50 wt.% monochlorobenzene, are metered into a circulating pump reactor.

- To maintain the alkalinity, 525 kg/h of 32% sodium hydroxide solution are metered in and the reaction mixture
25 is passed back to the pump via the heat exchanger and the detention tank, the above substance streams being metered in.

The temperature is 38°C.

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A part amount of the emulsion which is as high as that of the raw materials flowing in is fed before the metering points for BPA and phosgene from the detention tank to a

further pump and pumped through a tube reactor. 1,540 kg/h of sodium hydroxide solution (32 wt.%) and 966 kg/h of a solution (20 wt.%) of p-tert-butylphenol, dissolved in the solvent mixture, are metered into this stream. After a dwell time of 7 min, 55 kg/h of N-ethylpiperidine (0.026 mol per mol of bisphenol A) in the form of a 5.1% solution in the solvent mixture (50 parts methylene chloride and 50 parts monochlorobenzene) are metered in and the emulsion is pumped through a further tube reactor by means of a further pump.

After a dwell time of 7 min, the emulsion is separated in a separating vessel and the polycarbonate solution is washed free from electrolytes by known processes, e.g. by the centrifuge technique.

The polycarbonate solution is concentrated in evaporation units and freed from residual solvent on a devolatilization extruder.

The following analytical data are determined on the polycarbonate granules:

YI = 1.29
Eta rel = 1.194
Phenol. OH = 80 ppm
Nitrogen = 3 ppm

Comparison example 1

The polycarbonate is prepared as described in EP-A 1 249 493 (check 16.10.2002 Le A 34 952) example 3. 28 kg/h of

ethylpiperidine (0.0107 mol per mol of bisphenol A) are metered.

- 5 The following analytical data are determined on the polycarbonate granules:

YI = 1.4

Eta rel = 1.196

10 Phenol. OH = 90 ppm

(Nitrogen = 30 ppm

Comparison example 2

- 15 As described in example 1, but the following amounts are metered:

31,000 kg/h of BPA solution, 2,460 kg/h of phosgene, 523 kg/h of NaOH 32% in the circulating pump loop and 1,320 kg/h of NaOH 32% after the circulating pump loop, 857 kg/h of butylphenol solution (20%) and 24 kg/h of N-ethylpiperidine (0.0104 mol per mol of bisphenol A) (4.8% solution).

- 25 The following analytical data are determined on the polycarbonate granules:

YI = 1.45

Eta rel = 1.193

30 Phenol. OH = 70 ppm

Nitrogen = 35 ppm

Comparison example 3

As described in example 1, but the following amounts are metered:

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27,000 kg/h of BPA solution, 2,135 kg/h of phosgene, 416 kg/h of NaOH 32% in the circulating pump loop and 1,190 kg/h of NaOH 32% after the circulating pump loop, 740 kg/h of butylphenol solution (20%) and 21 kg/h of N-ethylpiperidine (0.0105 mol per mol of bisphenol A) (4.6% solution).

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The following analytical data are determined on the polycarbonate granules:

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YI = 1.38

Eta rel = 1.196

Phenol. OH = 75 ppm

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Nitrogen = 42 ppm

The experiments clearly demonstrate that, surprisingly, if the metering of catalyst falls below the minimum this leads to a higher content of nitrogen in the polycarbonate.

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Patent Claims

1. Process for the continuous preparation of polycarbonates which contain 3 to 20 ppm of bonded nitrogen by the method of the continuous two-phase interface process from diphenols, phosgene, chain terminators, catalyst and optionally branching agents in a mixture of aqueous-alkaline phase and organic solvent phase, characterized in that the metered amount of catalyst is an amount of 0.012 to 0.03 mol of catalyst per mol of diphenol employed.
2. Process for the preparation of polycarbonate by the phase interface process according to claim 1, characterized by the following process steps:
 - a) continuous bringing together of the organic phase and the aqueous phase in the circulating pump loop of a circulating pump reactor, during which an emulsion forms, optionally using a mixer, wherein the organic phase is a solvent which is suitable for the polycarbonate and already contains the phosgene and the aqueous phase comprises water and a mixture of alkali metal hydroxide solution and phenolic components comprising diphenol and optionally monophenol as a chain terminator,

wherein
 - b) a temperature of less than 60°C is established in the circulating pump reactor, the circulating pump reactor provides an average dwell time of at least 2 minutes and a part amount of the emulsion formed is removed continuously from the circulating pump reactor via the detention tank,

and
 - c) the part amount of this emulsion removed is then pumped through

tube reactors which are equipped with mixing and detention zones and provide a total dwell time of between 2 minutes and 40 minutes,

wherein

- 1) the ratio (expressed in moles/mole) of metered amount of phosgene to the amount of phosgene theoretically necessary to react all the diphenol and phenol is between 1.12 and 1.22,
- 2) phosgene solution and diphenol solution are metered here within the circulating pump reactor directly after the detention tank, before the pump, into the circulating pump loop, optionally via a mixer, and the chain terminator can also be conveyed into this circulating pump loop or optionally directly into the tube reactors, see 5),
- 3) within the circulating pump reactor alkali metal hydroxide solution is topped up in the circulating pump loop, after the detention tank but before the pump, in an amount of 15 - 40% of the total amount to be topped up,
- 4) within the circulating pump reactor diphenol and phosgene solutions are metered into the circulating pump loop according to 2) such that the part amount removed at the detention tank corresponds to the total amount of solutions metered in,
- 5) further 85 - 60% of the total alkali metal hydroxide solution to be topped up and optionally chain terminator are added into the part amount removed from the detention tank, directly before introduction into the tube reactor, and

- 6) after a further 1 - 20 minutes dwell time in the tube reactor, the catalyst is added in an amount of 0.012 to 0.03 mol of catalyst per mol of bisphenol employed.
3. Polycarbonate obtained by the process according to claim 1.
4. Shaped articles and extrudates of polycarbonate according to claim 3.
5. Optical data stores of polycarbonate according to claim 3.