

PROCESS FOR THE PREPARATION OF HIGH-PURITY BISPHENOL A

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FIELD OF THE INVENTION

The invention relates to a process and in particular to a process for preparing bisphenol A.

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BACKGROUND OF THE INVENTION

2,2-Bis(4-hydroxyphenyl)propane (bisphenol A, BPA), which is the condensation product of phenol and acetone, is a starting material or intermediate for the preparation of a large number of commercial products. Thus it is used as a starting material for the preparation of various types of polymeric materials, for example
15 polyarylates, polyetherimides, polysulfones and modified phenol-formaldehyde resins. Preferred fields of application are in the preparation of epoxy resins and polycarbonates.

Technically relevant methods of preparing BPA are known, e.g. WO 00/35847 and
20 US 2,775,620.

After the acid-catalyzed reaction of phenol with acetone, BPA is separated from the product mixture in the form of a crystalline adduct of BPA and phenol. Phenol is completely or partially removed from these crystals of BPA-phenol adduct by
25 distillative, desorptive or extractive methods. Before the separation from phenol, the crystals of BPA-phenol adduct may also be subjected to additional purification steps to reduce the concentration of secondary components.

The crystals of BPA-phenol adduct may be recrystallized e.g. from phenol, organic
30 solvents or mixtures of these solvents. The phenol present in the adduct crystals may also be completely or partially separated off here by the appropriate choice of solvents.

Thus PL 159620 describes a laborious process for the purification of bisphenol A wherein the crystals of BPA-phenol adduct isolated in a first stage are dissolved in phenol and the resulting solution is cooled in a batch crystallizer in a kind of static multilayer crystallization process, crystals of BPA-phenol adduct growing on the
5 tubes. When the mother liquor has been drained off, the crystals of BPA-phenol adduct recrystallized in this way are washed with phenol containing water in order to remove any mother liquor still adhering, and/or purified further by heating to a temperature of 75 to 85°C, i.e. by exudation. However, as the process has to be carried out batchwise, the equipment costs are correspondingly high. Moreover,
10 the production outputs based on the heat-transfer area are an order of magnitude lower in this process than in a continuous suspension crystallization of crystals of BPA-phenol adduct. Furthermore, an acceptable space-time yield requires high cooling rates, so a multilayer crystallization of this type has to take place at substantially higher crystal growth rates than a continuous suspension
15 crystallization. The resultant increased incorporation of impurities into the crystals has to be compensated by time-intensive exudation and/or washing operations. If a high purity is required, it may be necessary to use a multistage process.

EP 718 268 A describes a process for the preparation of a crystalline adduct of
20 bisphenol A and phenol wherein BPA dissolved in phenol is first crystallized out as an adduct and filtered off, and then redissolved in phenol, crystallized out again and filtered off, this step of the recrystallization being repeated several times. In the last step of the multistage recrystallization, the adduct is washed with specially purified phenol. The washing liquids and filtrates for washing and dissolving the
25 adducts are at least partially recycled.

WO 02/40435 describes a process wherein high-purity bisphenol A is obtained by multiple recrystallization from phenol and washing of the adducts in the individual stages with high-purity phenol in a cross-flow washing plant. The phenol used as
30 washing phenol contains virtually no bisphenol A or isomers thereof. A multiple

recrystallization is preferred. Washing with high-purity phenol at each of the individual stages requires a very large amount of high-purity phenol; furthermore, a large amount of bisphenol A is dissolved in the phenol at each individual stage, resulting in losses of yield.

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WO 03/82785 describes a process for the preparation of bisphenol A wherein in the first step a suspension of crystals of BPA-phenol adduct is filtered under vacuum and washed and the resulting filter cake is dissolved in a liquid containing phenol and crystallized again. The crystals obtained are separated off by

10 centrifugation. However, the continuous (filter) centrifuges that are more economic for larger plant capacities demand a minimum crystal size, which requires special crystallization procedures.

EP 1 367 043 A describes a process for the purification of bisphenol A wherein

15 the crystals of BPA-phenol adduct are dissolved in phenol and the resulting solution is filtered at least once before the crystals of BPA-phenol adduct are crystallized out again.

SUMMARY OF THE INVENTION

20 A process for the preparation of high purity bisphenol A is disclosed. The multi-step process entails a) reacting phenol with acetone in the presence of an acidic ion exchanger and a sulfur-containing co-catalyst to give a product mixture that includes bisphenol A and phenol; b) continuously obtaining from the product mixture crystals of bisphenol A-phenol adduct by suspension crystallization, c)

25 separating the adduct obtained in step (b) by solid-liquid separation to obtain a solid phase and a liquid phase d) washing of the solid phase with a solution containing phenol to obtain washed solid phase and a second liquid phase, e) distilling the liquid phase and said second liquid phase to obtain dewatered solution containing 5 to 15 % p,p-BPA, 3 to 12% isomers of BPA and less than

30 0.3% water, f) introducing of at least 90% by weight of the dewatered solution

into step (a), g) adding phenol to the washed solid phase obtained in step d) to obtain a homogeneous material system that contains p,p' -BPA, isomers of BPA and water h) continuously obtaining from the homogeneous material system crystals of bisphenol A-phenol adduct by suspension crystallization; i) separating
5 the crystals obtained in step (h) by solid-liquid separation to obtain a second solid phase, j) washing the second solid phase with a solution that contains phenol to obtain a washed adduct; and k) heating the washed adduct to remove phenol.

DETAILED DESCRIPTION OF THE INVENTION

- 10 The object of the present invention is to provide a simple process for the preparation of high-purity bisphenol, especially bisphenol A, with a purity of at least 99.8%, to give a low colour index and a high temperature stability in the melt.
- 15 A low colour index is understood as meaning a colour index of at most 20 Hazen units. To determine the colour index, 10 g of bisphenol A are melted under air in an oil bath at a temperature of 175°C over 20 minutes, after which the colour index is determined immediately according to ASTM D 1209. To determine the temperature stability, this material is then heated for 4.5 h at a bath temperature of
20 175°C, after which the colour index is measured again. A high temperature stability is understood as meaning that the colour index increases by at most 40 Hazen units.

The invention provides a process for the preparation of bisphenol A comprising
25 the following steps:

- a) reacting phenol with acetone in the presence of an acidic ion exchanger and a sulfur-containing co-catalyst to give a product mixture that includes bisphenol A, phenol, BPA isomers, un-
30 reacted acetone, and water;

- 5 b) continuously obtaining from the product mixture crystals of bisphenol A-phenol adduct by suspension crystallization in at least one crystallizer equipped with at least one heat exchanger, said product mixture containing 0.1 to 6 % by weight of water,
- c) separating the adduct obtained in step (b) by solid-liquid separation to obtain a solid phase and a liquid phase
- 10 d) washing of the solid phase with a solution containing phenol to obtain washed solid phase and a second liquid phase,
- e) distilling the liquid phase and said second liquid phase to obtain dewatered solution containing 5 to 15 wt.-% p,p-BPA, 3 to 15 12 wt.-% isomers of BPA yes and less than 0.3 wt.-% water, the percents relative to the weight of the dewatered solution,
- f) introducing of at least 90 wt.-% by weight of the dewatered solution into step (a),
- 20 g) adding phenol to the washed solid phase obtained in step d) to obtain a homogeneous material system comprising 15 to 35 wt.-% p,p' -BPA, 0.05 to 2 wt.-% of isomers of BPA and 0.1 to 10 wt.-% water
- 25 h) continuously obtaining from the homogeneous material system crystals of bisphenol A-phenol adduct by suspension crystallization in at least one crystallizer equipped with at least one heat exchanger;

- i) separating the crystals obtained in step (h) by solid-liquid separation to obtain a second solid phase,
- 5 j) washing the second solid phase with a solution that contains phenol to obtain a washed adduct; and
- k) heating the washed adduct to at least 120°C to remove phenol.

The process according to the invention affords a bisphenol A with a purity of at
10 least 99.8 wt-% of p,p-BPA, based on all the components contained in the product, except phenol.

In step (a) of the process according to the invention, the reaction of phenol and acetone takes place in the presence of an acidic ion exchanger and a sulfur-
15 containing co-catalyst to give a product mixture containing bisphenol A. Step (a) is based on the acid-catalyzed reaction of phenol with acetone, the phenol/acetone ratio in the reaction preferably being adjusted to at least 5:1. The reaction is conventionally carried out continuously and generally at temperatures of 45 to 110°C, preferably of 50 to 80°C. Acidic catalysts used are gel-like (microporous)
20 or macroporous sulfonated crosslinked polystyrene resins (acidic ion exchangers), which may be either monodisperse or heterodisperse. Divinylbenzene is normally used as the crosslinking agent, but other crosslinking agents, such as divinylbiphenyl, may also be used. The catalyst is used together with a co-catalyst, which conventionally is a thiol carrying at least one SH group and having a
25 positive influence on both the selectivity and the reactivity of the reaction. The co-catalyst may be either homogeneously dissolved in the reaction solution or fixed to the catalyst itself. Examples of homogeneous co-catalysts are mercaptopropionic acid, hydrogen sulfide, alkyl sulfides or alkylsilylthiols, such as ethyl sulfide or silylmethanethiol and similar compounds. Fixed co-catalysts are aminoalkylthiols
30 and pyridylalkylthiols ionically bonded to the catalyst, it being possible for the SH

group to be protected and to be freed only during or after fixation to the catalyst, e.g. as in the case of dimethylthiazolidine and alkylcarbamoylethylthio esters. The co-catalyst may also be covalently bonded to the catalyst as an alkylthiol or arylthiol, or be a constituent of the catalyst. It is also possible for two or more of
5 the co-catalysts described to be used together.

Apart from unreacted phenol and optionally acetone, the product mixture formed in the reaction of phenol with acetone in the presence of acidic catalysts contains essentially BPA and water. These are accompanied by small amounts of isomers
10 as typical by-products of the condensation reaction, examples being 2-(4-hydroxyphenyl)-2-(2-hydroxyphenyl)propane (o,p-BPA), substituted indanes, hydroxyphenylindanols, hydroxyphenylchromans, spiro-bis-indanes, substituted indenols, substituted xanthenes and more highly condensed compounds having three or more phenyl rings in the molecular skeleton. Other secondary
15 components, such as anisole, mesityl oxide, mesitylene and diacetone alcohol, may also form due to autocondensation of the acetone and reaction with impurities in the raw materials.

The reaction in step (a) may be carried out in such a way that the acetone is
20 completely converted. For economic and technical reasons, however, it is usually carried out so that, rather than 100% of the acetone being converted, up to 1.0 wt-% of acetone still remains in the reactor outflow.

The reaction may also take place in several reactors connected in series, the total
25 amount of acetone being distributed so that acetone is metered in before the reaction mixture enters each reactor.

Said by-products, as well as the unreacted starting materials such as phenol and acetone, detract from the suitability of BPA for the preparation of polymers and

have to be separated off by suitable processes because high purity demands are made on the BPA, especially for the preparation of polycarbonate.

- From the product mixture obtained in step (a), which contains 0.1 to 6 wt-% and preferably 0.5 to 2 wt-% of water, crystals of bisphenol A-phenol adduct are crystallized out in step (b) by continuous suspension crystallization. The product mixture obtained in step (a) is not subjected to distillation upstream of step (b) or (c) to remove readily volatile constituents (including water).
- 10 The crystallization may take place in one or more crystallizers connected in series. The mean total residence time of the crystals in this crystallization stage is preferably 30 minutes to ten hours. With a correspondingly slow crystallization, the inclusion of mother liquor and the incorporation of impurities into the crystals of BPA-phenol adduct may be avoided to the greatest possible extent. The cooling
- 15 is effected indirectly by means of heat exchangers. In the crystallization the product mixture is cooled to 40 to 50°C in one crystallization step. Preferably, however, the crystallization takes place in two steps, the product mixture being cooled to a temperature of 50 to 65°C in the first step and then to a temperature of 40 to 50°C in the second step. In both embodiments the cooling is effected by
- 20 means of one or more heat exchangers per crystallizer.

In one preferred embodiment the temperature of the product mixture is adjusted upstream of step (b) to a temperature that is at most 5°C above the crystallization point.

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The subsequent solid-liquid separation, especially filtration in step (c), and washing in step (d) may be carried out e.g. in or on one of the following types of apparatus: continuous filter centrifuges such as screen-conveyor centrifuges or pusher centrifuges, batch filter centrifuges such as skimmer centrifuges, and

continuous filters such as rotary or drum filters, belt filters and disk filters. It is preferable to use rotary filters and particularly vacuum rotary filters.

In the case of filtration by means of a vacuum rotary filter, the filtration is
5 preferably carried out as described in DE 199 61 521 A.

The washing of the solid phase, especially the filter cake, is effected with a phenolic solution, which extensively displaces the mother liquor remaining in the filter cake and frees the crystals of BPA-phenol adduct from impurities adhering to
10 the surface. The filter cake may be washed with a single phenolic solution or several phenolic solutions of different compositions, which are applied successively or as a mixture, e.g. via spray nozzles. Averaged over the total amount used, the phenolic solution preferably contains 84 to 99.45 wt-% of phenol, 0.5 to 15 wt-% of BPA and 0.05 to 1.1 wt-% of isomers. These
15 concentrations are based on the solution without taking water into account. The phenolic solution used contains 0.05 to 12 wt-% of water, preferably 0.2 to 3 wt-% of water, based on the total amount (of phenolic solution), and 5 to 100 wt-% thereof preferably originates from step (i) and/or (j). The temperature of the washing liquid is preferably 40 to 85°C and particularly preferably 45 to 70°C.
20 In the case of a rotary filter, part of the phenolic solution from step (i) and/or (j) may be used for rinsing the cloth of the rotary filter in step (c) and (d).

The adduct crystals obtained in step (d) in the form of a filter cake moistened with phenol preferably have a BPA purity of at least 99 wt-%, based on the sum of BPA
25 and secondary components. The residual moisture in the filter cake as a proportion by weight of the liquid adhering to the crystals of BPA-phenol adduct, based on the total weight of moist filter cake, is below 40 wt-% and preferably 15 to 30 wt-%. Preferably, the amount of phenolic solution for washing the filtered crystals of bisphenol A-phenol adduct is chosen so that the amount of washing liquid

corresponds to 20 to 120 wt-% of the amount of filtered crystals of BPA-phenol adduct. The amount used is preferably 50 to 90 wt-%.

Preferably, the water is completely or partially removed by distillation from the
5 liquid phase obtained in step (c) and (d) from the solid-liquid separation and/or the washing, especially down to a content of 0 to 0.3 wt-%, after which at least 90 wt-% thereof is recycled into step (a), optionally after the addition of acetone, phenol and/or a homogeneous co-catalyst. The recycled solution contains preferably 5 to 15 wt-% and particularly preferably 6.5 to 10 wt-% of p,p'-BPA and 3 to 12 wt-%
10 of isomers, obtained in step (e).

In the next step, (g), a homogeneous solution containing, inter alia, 15 to 35 wt-% and preferably 20 to 30 wt-% of BPA and 0.05 to 2 wt-% and preferably 0.1 to 1.1 wt-% of isomers is prepared by adding a phenolic solution to the crystals of
15 BPA-phenol adduct obtained in step (d). This is done by mixing the crystals of BPA-phenol adduct with a phenolic solution, the temperature of the resulting solution preferably being 70 to 100°C and being adjusted so that the homogeneous solution is subsaturated.

20 In one preferred embodiment, the crystals of BPA-phenol adduct moistened with phenol from step (d) are first melted to give a homogeneous melt having a temperature of 90 to 140°C and preferably of 95 to 130°C. A phenolic solution is then admixed. This procedure assures a thorough mixing and a rapid preparation of the BPA-phenol solution. It likewise avoids the situation where individual
25 contaminated crystals from the first crystallization step do not dissolve, causing contamination of the end product.

The amount of phenolic solution used in step (g) is adjusted so that the resulting homogeneous solution has a p,p'-BPA content of 15 to 35 wt-% and preferably of
30 20 to 30 wt-%. The concentration of isomers is 0.05 to 2 wt-%, preferably 0.1 to

0.8 wt-% and particularly preferably 0.2 to 0.5 wt-%. These concentrations are based on the solution without taking the water into account.

The homogeneous solution of BPA in phenol prepared in step (g) contains
5 preferably 0.1 to 10 wt-% of water and particularly preferably 0.2 to 3 wt-% of water. If the homogeneous solution were to contain no water, an increasing amount of acicular crystals would be obtained in the next step of the crystallization with the low concentrations of isomers in the mother liquor, and these crystals may lead to various problems in the plant, namely, inter alia,
10 accelerated fouling on cooling surfaces during the crystallization, and deterioration of the washing-out behaviour in the solid-liquid separation. This may detract from the product quality. The presence of water produces sturdy crystals, i.e. shorter and thicker crystals. Moreover, the presence of water in these concentrations during the crystallization has the effect of reducing the incorporation of impurities into
15 the crystals, allowing a further increase in product purity.

In another embodiment according to the invention, independently of the operating temperatures in the crystallizers, it is possible to add acetone in concentrations of 0 to 5 wt-%, based on the resulting mixture, as a further degree of freedom other
20 than the addition of water. This measure makes it possible, inter alia, to optimize the crystal morphology, the solid-liquid separation behaviour, the fouling tendency and the behaviour of the impurities in respect of incorporation into the adduct crystals, and to adjust the concentration of the mother liquor.

A continuous suspension crystallization of a BPA-phenol adduct from the
25 homogeneous solution obtained in step (g) is then carried out in step (h). Crystals of bisphenol A-phenol adduct are obtained in step (h) by continuous suspension crystallization from the homogeneous solution obtained in step (g), and these crystals are separated from the liquid phase by solid-liquid separation (step i), especially filtration, and then washed with a phenolic solution (step j)). The
30 cooling in step (h) is effected indirectly by means of heat exchangers.

- The crystallization may take place in one or more crystallizers connected in series. The mean total residence time of the crystals in this crystallization stage should preferably be between half an hour and ten hours. With a correspondingly slow
- 5 crystallization, the inclusion of mother liquor and the incorporation of impurities into the crystals of BPA-phenol adduct may be prevented to the greatest possible extent. In the crystallization the product mixture may be cooled to 35 to 55°C in one crystallization step, for example, it being possible for one or more crystallizers to be operated in parallel. Alternatively, the crystallization may take place in two
- 10 steps, the product mixture being cooled to a temperature of 45 to 70°C in the first step and then to a temperature of 35 to 55°C in the second step. In both embodiments the cooling is effected by means of one or more heat exchangers per crystallizer.
- 15 The details of an alternative embodiment of the two crystallization stages (b) and (h) are as follows: In the first crystallization stage (step (b)) the crystallization takes place in two steps in series, and in the second stage (step (h)) it takes place in one step in one or more crystallizers operated in parallel. A step within a crystallization stage is understood as meaning a crystallization in a specific
- 20 temperature range. A crystallization stage carried out in two steps in series is thus carried out in two different temperature ranges in succession. The stepwise crystallization in the first stage achieves a greater purity, whereas in the second stage, because of the lower isomer contents present and the increased fouling tendency associated therewith, a longer working life of the heat exchangers is
- 25 achieved by crystallization in one step.
- In one preferred embodiment the temperature of the product mixture is adjusted upstream of step (h) to a temperature that is at most 5°C above the crystallization point.

The subsequent solid-liquid separation step (i), especially filtration, and washing in step (j) are carried out e.g. in or on one of the following types of apparatus: continuous filter centrifuges such as screen-conveyor centrifuges or pusher centrifuges, batch filter centrifuges such as skimmer centrifuges, and continuous
5 filters such as rotary or drum filters, belt filters and disk filters. It is preferable to use rotary filters and particularly vacuum rotary filters. It is particularly preferable to use a type of apparatus that is also employed in step (c) and (d).

In the case of filtration by means of a vacuum rotary filter, the filtration is
10 preferably carried out as described in DE 199 61 521 A.

The washing of the solid phase, especially the filter cake, is effected with a phenolic solution, which extensively displaces the mother liquor remaining in the filter cake and frees the adduct crystals from impurities adhering to the surface.
15 The solid phase, especially the filter cake, may be washed with a single phenolic solution or several phenolic solutions, which are applied successively or as a mixture, e.g. via spray nozzles.

The phenolic solution used for washing the recrystallized crystals of BPA-phenol adduct in step (j) may be either fresh phenol, i.e. commercially available phenol, or recycled phenols obtained in the plant, or mixtures of the two. A recycled phenol is understood as meaning a phenol that is obtained in the course of the process and recycled into the process. It is also possible to use phenols obtained in the preparation of polycarbonate by the melt process. The washing phenol used
20 here preferably contains in total a maximum of 1.0 wt-% of other phenolic components, e.g. isopropenylphenol, BPA and its isomers and secondary components. Recycled phenols, e.g. from the removal of phenols from the crystals of BPA-phenol adduct, are purified here only by distillation, if at all. The temperature of the washing phenol is 41 to 75°C and preferably 45 to 60°C. The
25 washing phenol may contain up to 10 wt-% of water.
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The adduct crystals obtained in step (j) in the form of a solid phase moistened with phenol, especially a filter cake moistened with phenol, preferably have a BPA purity of at least 99.8 wt-%, based on the sum of BPA and secondary components.

- 5 The residual moisture in the filter cake as a proportion by weight of the liquid adhering to the crystals of BPA-phenol adduct, based on the total weight of moist filter cake, is below 40 wt-% and preferably 15 to 30 wt-%. Preferably, the amount of phenolic solution for washing the filtered crystals of bisphenol A-phenol adduct is chosen so that the amount of washing liquid corresponds to 20 to 120 wt-% of
10 the amount of filtered crystals of BPA-phenol adduct. The amount used is preferably 50 to 90 wt-%.

- The liquid phase from (i) and (j), especially the filtrate, from the solid-liquid separation of the second crystallization stage, (i), is used in step (g) for mixing
15 with the molten filter cake from (d), and in step (c) for washing the filter cake and/or for rinsing purposes (e.g. washing the cloth), optionally after the addition of water and/or acetone. Preferably 10 to 50 wt-% and particularly preferably 20 to 40 wt-% of the liquid phase obtained in step (i) and/or (j) is recycled into step (d) for washing purposes. Also, preferably 50 to 90 wt-% and particularly preferably
20 60 to 80 wt-% of the filtrates obtained in step (i) and/or (j) is used in step (g).

- In one preferred embodiment, all or part of the mother liquor obtained in step (i) and of the washing and dehumidifying filtrates (j) may be collected separately. The filtrates from washing and dehumidified, which are less contaminated with
25 isomers, are preferably passed to step (g), while part of the mother liquor is preferably passed to step (d). Due to the increased discharging of the isomers, their concentration level drops in the second crystallization stage, thereby improving the product purity. Dehumidifying filtrates are understood to be those filtrates which are removed from the filter cake as residual washing liquids on applying a
30 vacuum of 5 to 500 mbar.

Another possible way of lowering the isomer concentration in the second crystallization stage, (h), and thereby increasing the resulting product purity consists in evaporating 0 to 35 wt-%, preferably 0 to 10 wt-%, of the filtrates obtained in step (i) and/or (j), passing the bisphenol A and isomer-free top
5 product, consisting essentially of phenol, water and optionally acetone, to step (g) and/or step (j), optionally after further purification, and recycling the bottom product, enriched in bisphenol A and isomers, upstream of step (b). This measure affords better control over the phenol balance of the plant and hence improves operability.

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An alternative embodiment of the process comprises the preparation of BPA in two categories of purity, namely a BPA with a purity of 99.5 to 99.75 wt-% and a high-purity BPA with a purity of at least 99.8 wt-%, in one plant. In this case both the one-stage and the two-stage crystallization, as well as the subsequent product
15 work-up (solid-liquid separation, washing, dissolution, and removal of phenol), are carried out separately for the different BPA purities. However, the mother liquors from the first crystallization stage and first solid-liquid separation stage may be processed together and recycled into the reaction, the product mixture formed in the reaction then being subjected to separate crystallization and product
20 work-up for the different BPA purities.

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In step (k) phenol from the solid phase obtained in step (j), especially the filter cake, is removed from BPA-phenol adducts by thermal separation at temperatures of at least 120°C. Preferably, the phenol is completely or partially removed by
distillative and/or desorptive methods such as those described e.g. in
DE 198 48 026 A, DE 198 60 144 A and DE 199 61 566 A.

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The process according to the invention makes it possible to prepare bisphenol A with a purity of at least 99.8 wt-% of p,p-BPA, a low colour index and a high temperature stability.

After the phenol has been separated off to levels preferably of max. 600 ppm and particularly preferably of max. 100 ppm in step (k), a bisphenol A melt is obtained which may be used, optionally without prior solidification, for the preparation of polycarbonate by the transesterification process (melt polycarbonate). However, 5 the bisphenol A melt may also be solidified by known processes such as the prilling process, or by exfoliation, for sale or further utilization. Furthermore, the melt may be dissolved in sodium hydroxide solution and used for the preparation of polycarbonate by the phase boundary method.

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This gives a polycarbonate with a low yellowness index (YI) of max. 1.5 as a measure of the colour.

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In another embodiment of the process, the melt is evaporated in step (k) to residual phenol contents of 2 to 20 wt-%, as described in DE 199 54 787 A, and this melt, without prior solidification, is reacted with diphenyl carbonate by the melt process to give polycarbonate. This again yields a polycarbonate with a low YI.

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The liquid phase obtained from the solid-liquid separation in step (c) and (d) (mother and washing liquor) contains phenol, BPA, water and optionally acetone and co-catalyst, and is enriched in the secondary components typically obtained in the preparation of BPA. The water is separated from the liquid phase obtained in step (c) and (d) (mother and washing liquor) to residual contents of max. 0.3 wt-%, preferably of 0.25 wt-%, and at least 90 wt-% of the resulting solution is 25 recycled into the reaction in step (a), with the optional addition of acetone, phenol and co-catalyst.

30

With an increasing concentration level of water and/or optionally acetone in the second crystallization stage, (h), it may be advantageous to carry out a thermal separation of these components from the phenolic solution transferred from step

(i) and (j) to step (d), and optionally to recycle the resulting distillate into the second crystallization step (in or upstream of step (h)), especially if the concentration of these compounds in the second crystallization stage becomes so high that a separate evaporation or distillation of the solutions transferred from step (i) and (j) to step (d), as a rough separation, offers economic advantages compared with the separation of water in the main circuit.

After work-up of the material stream between step (c) and (d) and step (a) in order to remove water, a partial stream of 0.5 to 10 wt-%, or so-called discharge, is taken off. This partial stream is withdrawn from the process chain as so-called BPA resin, optionally after the recovery of phenol, isopropenylphenol, bisphenol A or other components and optionally after prior treatment with acid(s) and/or base(s).

By way of example, the discharge may be subjected first to rearrangement on an acidic ion exchanger, then to concentration by partial distillation of the phenol, and then to crystallization and filtration. The distillate obtained may be used to wash the filter cake and rinse the cloth. The crop of crystals containing BPA may be recycled into the first crystallization stage, (b), and the isomer-enriched mother liquor may be worked up further, preferably by distillation, to recover more phenol.

EXAMPLES

Example 1 a): Embodiment

A product mixture obtained in step (a), containing 70.1 wt-% of phenol, 22.0 wt-% of BPA, 6.6 wt-% of isomers, 1.1 wt-% of water and 0.2 wt-% of acetone, was introduced continuously into a crystallizer for the purpose of suspension crystallization in step (b) (1st crystallization stage). The mean residence time in the crystallizer was 1 h and the mixture was circulated through an external heat exchanger. The temperature of the crystallizer was thus adjusted to 41°C. The

crop of crystals found under steady-state conditions had the phenol-free composition shown in Table 1, row 1. A sturdily acicular crystal habit was found.

5 The crystals of BPA-phenol adduct filtered off step (c) and washed in step (d) were melted and mixed with a phenolic solution in step (g) to form a homogeneous solution containing 77 wt-% of phenol, 22 wt-% of BPA and 1 wt-% of isomers, as shown in Table 1, row 2.

10 This homogeneous solution shown in Table 1, row 2 was mixed with water in a ratio of 99:1 and crystallized under the conditions described (residence time 1 h, external heat exchanger, temperature 41°C) (2nd crystallization stage, step (h)). The crystals of BPA-phenol adduct found under steady-state conditions after filtration (i) and washing in step (j) had the phenol-free composition shown in Table 1, row 4. A sturdy, slightly acicular crystal habit was found.

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Example 1 b): Comparative Example

20 A product mixture obtained analogously to step (a), containing 70.1 wt-% of phenol, 22.0 wt-% of BPA, 6.6 wt-% of isomers, 1.1 wt-% of water and 0.2 wt-% of acetone, was introduced continuously into a crystallizer for the purpose of suspension crystallization (1st crystallization stage). The mean residence time in the crystallizer was 1 h and the mixture was circulated through an external heat exchanger. The temperature of the crystallizer was thus adjusted to 41°C. The crop of crystals found under steady-stage conditions had the phenol-free composition shown in Table 1, row 1. A sturdily acicular crystal habit was found.

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The filtered and washed crystals of BPA-phenol adduct were melted and mixed with a phenolic solution to form a homogeneous solution containing 77 wt-% of phenol, 22 wt-% of BPA and 1 wt-% of isomers, as shown in Table 1, row 2.

This homogeneous solution was crystallized under the conditions described above (residence time 1 h, external heat exchanger, temperature 41°C) in a suspension crystallization without the presence of water (2nd crystallization stage). The crystals of BPA-phenol adduct found under steady-state conditions after filtration and washing had the phenol-free composition shown in Table 1, row 3. A distinctly acicular crystal habit was found. The product purity was lower than in Example 1 a) according to the invention.

Table 1

Purity of the crystals of BPA-phenol adduct without taking the phenol into account, and composition of the recrystallization feed

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	Phenol [wt-%]	p,p-BPA [wt-%]	Isomers [wt-%]
1. crystallized once		99.29	0.71
2. recrystallization feed	77	22	1
3. recrystallized (Comparative Example 1 b))		99.84	0.16
4. recrystallized, addition of water (Embodiment 1 a))		99.88	0.12

Example 2:

A phenolic solution containing 4 wt-% of acetone, max. 0.1 wt-% of water, 9 wt-% of p,p'-BPA and isomers was reacted in step (a) at a rate of 50 t/h in the
10 presence of an ion exchange resin in sulfonic acid form and mercaptopropionic acid as co-catalyst. The reaction product contained about 24 wt-% of p,p'-BPA.

After the addition of a partial stream enriched in p,p'-BPA from steps (c) and (d) and (i) and (j), BPA-phenol adduct was crystallized continuously from the
15 resulting mixture in a first crystallization stage, (b), in two steps at 54°C and 41°C with a total residence time of 8 h, the suspension being cooled and the heat of crystallization dissipated by means of heat exchangers.

The solid-liquid separation of the suspension in step (c) was carried out on a
20 vacuum rotary filter, the resulting filter cake as well being washed with a phenolic solution at about 55°C in step (d).

The filter cake was first melted and then mixed with a phenolic solution to give a homogeneous solution in step (g). The solution prepared in this way contained 25 wt-% of p,p'-BPA and 0.3 wt-% of isomers. Water was added before crystallization to give a water content of 1 wt-% in the homogeneous solution. The temperature of the solution was adjusted to 79°C.

The repeat crystallization in step (h) was carried out continuously in two steps at 54°C and 41°C, the suspension being cooled and the heat of crystallization dissipated by means of heat exchangers in each case. The residence time in this crystallization stage (h) was 4 h.

In step (i) the suspension was filtered on a vacuum rotary filter and washed (j) at about 55°C with a phenolic solution containing max. 0.1 wt-% of isomers.

The resulting crystals of BPA-phenol adduct moistened with phenol, having a residual moisture content of about 25 wt-%, were then melted and the phenol was removed by thermal separation in step (k) to a content of 90 ppm. After prilling of the BPA melt, the BPA obtained had a purity of at least 99.9% and a colour index of less than 20 Hazen units.

The mother liquor from steps (c) and (d) and (i) and (j) was extensively dewatered. A partial stream was taken from the dewatered mother liquor and subjected to distillation of the part of the phenol. The distillate was used to wash the filter cake and rinse the cloth. After further separation by means of crystallization and filtration, a BPA-containing stream from the BPA-enriched bottom product was recycled into the first crystallization stage, (b), and the isomer-enriched mother liquor was worked up further to recover phenol.

Example 3: Simulation of a two-stage crystallization process

A simulation study of a two-stage crystallization process for the preparation of high-purity bisphenol A is described below. The simulations were performed using the commercial software package Aspen Custom Modeler®. The software is based on a process model with special models for the reaction (detailed reaction kinetics), for the kinetics of the incorporation of impurities in the crystallization, and for other basic operations.

Step (a): Reaction of acetone and phenol to give p,p'-BPA and isomers, with the formation of water, in adiabatic fixed bed reactors in the presence of a co-catalyst under the following inflow conditions:

4 wt-% of acetone, 0.07 wt-% of water, 9 wt-% of p,p'-BPA;
temperature: 52°C.

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Step (b): The reaction products, containing 22.5 wt-% of p,p'-BPA, were passed to the first crystallization stage, where BPA-phenol adduct was crystallized in two steps at 54°C and 41°C with a total residence time of 5 h. The calculated purity of the crystals was 99.68 wt-%, based on bisphenol A.

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Step (c): The suspension was filtered through a vacuum rotary filter,

Step (d): washed and dehumidified on the same vacuum rotary filter. The filter cake was washed using a partial stream of 27% of the filtrates from step (i) and (j), corresponding to a ratio of amount of washing liquid to amount of resulting solid of 0.9.

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The phenolic mother liquor discharged from the recrystallization stage contained 9 wt-% of p,p'-BPA, 0.3 wt-% of isomers and 1.3 wt-% of water. Some of this

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partial stream was used together with recycled phenols from the plant to clean the filter cloth.

5 The dehumidified filter cake had a residual moisture content of 25 wt-%. With the impurities from the mother liquor still adhering to the crystals, and from the isomer-laden washing liquid, the purity of the filter cake after leaving the rotary filter was 99.4 wt-%, based on p,p'-BPA.

10 Step (g): The filter cake from (d) was melted and mixed with the residual filtrates from (i) and (j) so that the concentration of p,p'-BPA in the inflow of the second crystallization stage, (h), was 23 wt-%. The solution formed also contained 0.3 wt-% of isomers and 1 wt-% of water.

15 Step (h): Crystallization in two steps at 54°C/41°C with a total residence time of 5.5 h. The calculated purity of the adduct crystals was 99.93 wt-%, based on p,p'-BPA.

20 Step (i): The suspension obtained was filtered step

25 Step (j): washed with fresh phenol and recycled phenol streams from the plant, and then dehumidified. Part of these phenol streams used in step (j) for washing was also used to clean the filter cloth. The amount of washing liquid used to wash the filter (j) cake was 71 wt-%, based on the solid obtained. The filtrates obtained from filtration and washing in step (i) and (j) were combined and recycled into steps (d) and (g) together with the filter cloth clearing liquor.

30 Step (k): The filter cake, with a residual moisture content of 25 wt-%, was melted. The phenol content was reduced by means of thermal

separation to a residual value of 150 ppm in the BPA melt. The resulting phenol was passed to step (j). The BPA melt obtained had a purity of 99.92 wt-%, based on p,p'-BPA.

- 5 The mother and washing liquor from step (c) and (d) was dewatered to a water content of 0.075 wt-%. A partial stream thereof, corresponding to 4% of the total amount, was taken off in order to discharge the isomers as BPA resin after downstream recovery of the phenol. The remaining part of the dewatered mother liquor was recycled into the reaction in step (a), with the addition of acetone,
10 phenol and a co-catalyst.

- According to the simulation study, the impurity content of the product decreased by 12% if the filtrates from filtration and washing in step (i) and (j) were not combined but separated in such a way that the mother liquor more heavily laden
15 with isomers (filtrate from the filtration (i)) was preferably passed to step (d) and the washing filtrates from (j) were preferably passed to step (g).

- Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and
20 that variations may be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. Process for the preparation of bisphenol A comprising the following steps:
 - 5 a) reacting phenol with acetone in the presence of an acidic ion exchanger and a sulfur-containing co-catalyst to give a product mixture that includes bisphenol A, phenol, BPA isomers, unreacted acetone, and water;
 - 10 b) continuously obtaining from the product mixture crystals of bisphenol A-phenol adduct by suspension crystallization in at least one crystallizer equipped with at least one heat exchanger, said product mixture containing 0.1 to 6 % by weight of water,
 - 15 c) separating the adduct obtained in step (b) by solid-liquid separation to obtain a solid phase and a liquid phase
 - d) washing of the solid phase with a solution containing phenol to obtain washed solid phase and a second liquid phase,
 - 20 e) distilling the liquid phase and said second liquid phase to obtain dewatered solution containing 5 to 15 wt.-% p,p-BPA, 3 to 12 wt.-% isomers of BPA and less than 0.3 wt.-% water, the percents relative to the weight of the dewatered solution,
 - 25 f) introducing of at least 90 wt.-% by weight of the dewatered solution into step (a),
 - g) adding phenol to the washed solid phase obtained in step d) to
30 obtain a homogeneous material system comprising 15 to 35 wt.-%

p,p' -BPA, 0.05 to 2 wt.-% of isomers of BPA and 0.1 to 10 wt.-% water

5 h) continuously obtaining from the homogeneous material system crystals of bisphenol A-phenol adduct by suspension crystallization in at least one crystallizer equipped with at least one heat exchanger;

10 i) separating the crystals obtained in step (h) by solid-liquid separation to obtain a second solid phase,

j) washing the second solid phase with a solution that contains phenol to obtain a washed adduct; and

15 k) heating the washed adduct to at least 120°C to remove phenol.

2. The process according to Claim 1 characterized in that 50 to 90 wt.-%, preferably 60 to 80 wt.-%, of the liquid phase obtained in sum in step (i and j) is used in step (g).

20 3. The process according to Claim 1 characterized in that 10 to 50 wt.-%, preferably 20 to 40 wt.-%, of the liquid phase obtained in sum in step (i and j) is recycled into step (d) for washing purposes.

25 4. The process according to Claim 1 wherein the solution that contains phenol referred to in step (j) contains no more than 1.0 % by weight of other phenolic components.

5. The process according to Claim 1 wherein the washed solid phase obtained in step d) is first melted before phenol is added to it in step g).

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6. The process according to Claim 1 where in at least one of step c) and i) the solid-liquid separation is carried out in a vacuum rotary filter.
- 5 7. The process according to Claim 1 wherein the solution containing phenol of step (d) contains 84 to 99.45 wt.-% of phenol, 0.5 to 15 wt.-% of BPA and 0.05 to 1.0 wt.-% of BPA isomers, the percents based on the weight of the solution except for the weight of the water.
- 10 8. The process according to Claim 1 characterized in that the solution containing phenol of step (d) contains 0.05 to 12 wt.-% of water the percent based on the total weight of said solution .
- 15 9. The process according to Claim 1 wherein 5 to 100 wt.-% of the solution containing phenol of step (d) originates from step (i) and (j).
- 20 10. The process according to Claim 1 wherein the crystallization of step (b), is carried out in two steps in series at temperatures that differ one from the other, and where the crystallization of step (h) is carried out in one step in two or more crystallizers operating in parallel.
- 25 11. The process according to Claim 1 wherein the material system of step g) contains max. 5 wt.-% acetone, the percent relative to the weight of the system.
- 30 12. The process according to Claim 1 characterized in that at least part of the liquid phase from the solid-liquid separation (step (i)) and at least part of the liquid phase from the washing in step (j) are collected separately, at least part of the liquid phase from the solid-liquid separation is recycled into step (d) and preferably at least part of the liquid phase from the washing is recycled into step (g).

13. The process according to Claim 1 characterized in that 0 to 35 wt.-%, preferably 0 to 10 wt.-%, of the liquid phases obtained in step (i and/or j) is evaporated, the top product is passed to step (d) and/or step (f) and the bottom product is recycled upstream of step (b).
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