

Description

The present invention relates to a process for the preparation of crystals of an adduct of a bisphenol and a phenol.

5 The purification of bisphenols by adduct crystallization has been practiced for some time with considerable variation. U.S. patent specification 2,791,616 discloses a process for crystallizing a bisphenol adduct and extracting the bisphenol with added water but this requires excessive amounts of water to produce increased yield. U.S. patent specification 3,936,507 discloses the crystallization of dried crude bisphenol with certain solvents in certain ratios. U.S. patent specification 4,192,955 discloses a process for crystallizing a bisphenol
10 from a solution in a solvent in which the bisphenol is soluble and which is miscible with water. U.S. patent specification 3,535,389 discloses crystallization from a two-phase mixture containing water and an organic solvent. U.S. patent specification 4,294,993 discloses treating bisphenol adduct with toluene or toluene and water, heating and cooling but toluene is too miscible with phenol to serve as an inert diluent coolant. Russian patent specification 798,085 discloses the use of an organic solvent added prior to condensation, such as 50% toluene
15 or benzene and optionally residual water. U.S. patent specification 4,209,646 describes a process for crystallizing a hot bisphenol adduct from a solution thereof in aqueous phenol by evaporating water to cool the liquid mixture at very reduced pressure to a point corresponding to the vapor pressure of the reaction mixture but this requires impractical amounts of energy to lower the pressure to the necessary very low level. Also, the patent states that the water content is critical and should be between 2-12% weight and, preferably, 4-8% weight. U.S. patent specification 4,492,807 discloses a process for crystallizing a bisphenol adduct from a liquid
20 mixture which includes water and an organic liquid which will not react with the bisphenol or phenol and is a solvent for dissolving a substantial portion of the impurities or by-products resulting from the formation of the bisphenol. The process allows crystallization at lower temperature. However, some of the solvents would likely introduce impurities and Applicant has found that the use of solvents of the patent to remove impurities did not lead to an increase in purity, size or processability of the adduct crystals.

Despite the many varied processes, including those described above, there is still a need to develop a process for the recovery of a bisphenol which provides high purity crystals of bisphenol adduct which are large and firm so that they are easier to wash and otherwise work up because they do not break in handling. It is also desirable to reduce the use of pump-circulated surface heat exchange systems and the problems associated with such surface heat exchange systems, including fouling, breaking of crystals, and induced nuclea-
30 tion of the crystals making them difficult to filter.

The present invention is directed to a process for the preparation of crystals of an adduct of a bisphenol with a phenol which comprises:

- 35 (a) adding 8-25% by weight of an inert volatile liquid aliphatic hydrocarbon diluent and 0 to 1.5% by weight of water to a crude mixture of the bisphenol and the phenol at a temperature above the boiling temperature of the added volatile liquid diluent; and
- (b) allowing the added volatile liquid diluent to boil in the process thereby cooling the resulting mixture from (a) to a temperature at which crystals of the adduct form.

The process of the invention provides a useful and efficient means of obtaining an adduct of a bisphenol
40 by a crystallization process in which the heat of crystallization of the adduct is removed, preferably without the direct contact with an external cooling means, such as direct surface heat exchange devices, and their associated problems while providing crystals of the desired adduct, which are increased in desirable size, purity and processability.

Any liquid can be used as the inert volatile liquid aliphatic hydrocarbon diluent which is inert to the other
45 ingredients, has a boiling point below the boiling point of the phenol, is stable and which does not substantially dissolve or would not be dissolved in the bisphenol (i.e., a solubility for bisphenol at 25 °C of about 500 ppm or less, preferably 300 ppm or less) or the bisphenol by-product impurities (i.e., a solubility at 25 °C of less than about 0.1% weight of the impurities, or even less than 0.03% weight. Examples of suitable liquid diluents include aliphatic hydrocarbons such as butanes, pentanes, hexanes, heptanes, and the like. Such materials
50 usually have a solubility in the mother liquor of 8-20% weight, preferably 10-15% weight at 45 °C. Operating at about the saturation point of the solvent in the mother liquor is useful. Preferably, the inert volatile liquid hydrocarbon diluent is an aliphatic hydrocarbon containing from 4 to 6 carbon atoms, especially pentane.

The amount of inert volatile liquid hydrocarbon diluent used can readily be determined by those skilled in the art for the particular size and kind of process used. By way of illustration, the amount of the inert volatile
55 liquid hydrocarbon diluent can be from 8 to 25% weight based on the total mixture of ingredients present in the crystallizer and, preferably, from 10 to 20% weight and, especially, from 10 to 15% weight based on the total mixture.

The present invention is useful for the purification of bisphenols from the conventional preparation of bi-

sphenols from a ketone and a phenol in the presence of an acid or an acidic acting material, including inorganic or organic materials in liquid or solid form. The bisphenols include those prepared by the reaction of a ketone, such as acetone, ethyl methyl ketone, isobutyl methyl ketone, acetophenone, cyclohexanone, 1,3-dichloroacetone, with a phenol, such as phenol, o-cresol, m-cresol, o-chlorophenol, m-chlorophenol, o-t-butylphenol, 2,5-xylene, 2,5-di-t-butylphenol, o-phenylphenol.

A typical feed stream to the crystallizer is a product from the conventional condensation of acetone with phenol to form 2,2-bis(4-hydroxyphenyl)propane, also called bisphenol A (BPA) and usually contains from about 15 to about 60% weight of the bisphenol A, preferably 15-25% weight, and the remainder unreacted acetone or phenol and by-products of the reaction, including undesired isomers of the desired bisphenol A, higher condensation products, and water. Usually, the bisphenol A product is distilled to remove acetone, water and excess phenol so that the feed stream contains about 35% bisphenol A and about 65% phenol and impurities.

While the process can be conducted in the presence of less than 1.5% by weight of water, preferably, less than 1% weight, or in the absence of water, the use of a small amount of water in the range of from 0.25 to 1.5% weight based on the mother liquor to the crystallizer, preferably from 0.3 to 1.0% weight, will usually result in larger crystals. Use of the lower amounts of water could result in a somewhat smaller crystal size than if the higher amounts of water are used. Higher amounts of water result in a lower freezing point of the bisphenol and therefore lower operating temperatures.

The temperature of the process is sufficiently high to provide for the boiling of the volatile liquid and yet cool enough by boiling of the volatile liquid, preferably in the absence of external cooling means, for the crystallization of the desired adduct. By way of illustration, when using hexane, the temperature is conveniently between 40 °C and 70 °C and, preferably between 45 °C and 65 °C. Operating at the lower range of temperatures could result in less impurities.

The pressure of the process is determined by the standard vapor pressure curve for the composition of the crystallizer admixture containing the volatile liquid diluent (and any water,) and the temperature of the crystallizer and generally does not require that the pressure of the process be extremely high. By choice of conditions, the process can be operated without substantially reducing the pressure below atmospheric pressure. The pressure can usually be about atmospheric pressure but can be any pressure at which the volatile liquid diluent (and any water) can function in the manner previously described to produce the desired cooling. By way of illustration, when using hexane as the volatile liquid and water in the amounts described above, the pressure can be from 35 to 350 kPa (absolute), preferably 35 to 140 kPa and butanes would require from 280 kPa to 1200 kPa. At the same diluent and water concentrations, pentanes would require higher pressures than hexane of from atmospheric to 630 kPa, preferably to 280 kPa. Heptanes would require pressures of from 14 to 140 kPa, preferably to 40 kPa. The use of atmospheric pressure $\pm$ 70 kPa is preferred.

The inert volatile liquid aliphatic hydrocarbon diluent can also serve a side benefit of reducing the density of the mother liquor and therefore improving the ability to separate the adduct crystals by centrifugation. It also lowers mother liquor viscosity.

The process can be conducted as a batch process or, preferably as a continuous process. One of skill in the art can readily adjust the rate of mixing and residence time to achieve the desired adduct crystals. Larger crystals are usually favored by longer residence times.

The adduct is recovered by conventional techniques known in the art as by filtration or, preferably by centrifugation or the like. Adduct crystallization can be conducted in one or more stages, with washing and redissolving in hot phenol between stages. The bisphenol is recovered from the adduct crystals by distillation of the phenol and cooling of the resulting molten bisphenol to a solid. Further purification can be accomplished by the same or another conventional crystallization method.

The mother liquor obtained after recovery of the adduct can be further crystallized to obtain residual bisphenol. Usually it is desirable to treat this mother liquor to remove excess aqueous phenol prior to the further crystallization. The mother liquor is then recycled with diluent (pentane) removal to the condensation reactor or used as a wash for earlier stage adduct crystals.

The inert volatile liquid is recovered by conventional procedures of condensation and the condensed volatile liquid is preferably recycled to the crystallization zone.

Example 1

A 65 litre, continuous stirred tank crystallizer operated with the stirrer at 120-700 rotations per minute was continuously injected with a crude phenol and bisphenol A mother liquor containing from 19-23% weight of bisphenol A (BPA). A second continuous feed of inert volatile liquid diluent, hexane, equal to from 9-13% by weight based on the total ingredients of the crystallizer admixture was added and the water content was varied based on the total feed to the crystallizer. The temperature was maintained at 48-60 °C and the residence time was

1-8 hours. The pressure was 70 kPa. The hexane vapor from the reflux cooling was condensed and recycled. The adduct crystals were recovered by filtering slurry samples under isothermal conditions and quickly washing them with toluene to displace the traces of mother liquor. Air was drawn through the cake to vaporize the toluene and the dried cake was weighed to give a conservative measure of the slurry concentration. Some of these cakes were analyzed for purity and size distribution. Results of experiments conducted under these conditions are set forth in Table 1 below.

Table 1Combined Feed Composition, %weight

Phenol	66.1	66.9	68.7	66.7
BPA	20.7	20.9	20.6	20.9
o,p'-isomer of BPA	2.0	2.0	2.0	2.0
Total				
Impurities ⁽²⁾	3.0	3.0	3.0	3.0
H ₂ O	0.58	0.55	1.0	0.58
Hexane	9.6	8.7	9.6	8.8

Stage 1 ResultsConditions

Temp., °C	60	60	60	60
Residence Time, h	2.1	1.5	2.1	1
Stirrer, rotations per min.	700	700	700	700

Adduct Analysis, Phenol-Free Basis

o,p'-isomer of BPA (ppm)	267	301	334	420
Total				
Impurities ⁽²⁾ (ppm)	544	593	609	734

Slurry Conc., 1st stage

%weight	11.2	11	9.8	11.4
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Estimated Average Crystal Size

(Visual) (micrometre)	150	150	150	100
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Stage 2 Results

Temp., °C	48	48	48	48
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Adduct Analysis, Phenol-Free Basis

o,p'-isomer of BPA (ppm)	332	355	(1)	-
Total				
Impurities ⁽²⁾ (ppm)	624	655	-	-

Slurry Conc., 2nd stage

%weight	20.8	17.6	-	-
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(1) No test

(2) includes o,p'-isomer of BPA

Results of the above experiments demonstrate that crystals of bisphenol A adduct were very pure and of increased size (width 75-150 vs 50 micrometres by conventional surface cooling processes) while the heat of crystallization due to adduct formation was removed without the use of direct contact with an external heat exchanger system.

Example 2

Experiments similar to those described in Example 1 were conducted utilizing water and pentane.

The function of pentane in the above experiments was primarily to remove heat of adduct crystallization by vaporization instead of by use of direct contact with an external surface cooling means. Pentane also acts as an inert diluent (due to limited solubility in phenol) and lowers the cloud point of the crystallizing mixture by approximately 8 °C in the relative absence of water. The end crystallization temperatures are lowered proportionately and adduct recovery remains about the same as in the previous example.

Claims

1. A process for the preparation of crystals of an adduct of a bisphenol with a phenol which comprises:
 - (a) adding 8-25% by weight of an inert volatile liquid aliphatic hydrocarbon diluent and 0 to 1.5% by weight of water to a crude mixture of the bisphenol and the phenol at a temperature above the boiling temperature of the added volatile liquid diluent; and
 - (b) allowing the volatile liquid diluent to boil in the process thereby cooling the resulting mixture to a temperature at which crystals of the adduct form.
2. A process according to claim 1 wherein the inert volatile liquid hydrocarbon diluent is an aliphatic hydrocarbon containing 4 to 6 carbon atoms.
3. A process according to claim 2 wherein less than 1% weight water is present in the resulting mixture.
4. A process according to claim 3 wherein the inert volatile liquid hydrocarbon diluent is butane or hexane.
5. A process according to claim 3 wherein the inert volatile liquid hydrocarbon diluent is pentane.
6. A process according to claims 1 to 5 wherein 0.25 to 1.5% weight water is present based on the mother liquor.
7. A process according to claim 6 wherein 0.3 to 1.0% weight water is present.
8. A process according to claims 1 to 7 wherein the bisphenol is bisphenol A.

Patentansprüche

1. Ein Verfahren zur Herstellung von Kristallen eines Addukts eines Bisphenols mit einem Phenol, umfassend:
 - (a) das Zugabe von 8 bis 25 Gewichtsprozent eines inerten, flüchtigen, flüssigen, aliphatischen Kohlenwasserstoffverdünnungsmittels und 0 bis 1,5 Gewichtsprozent Wasser zu einer Rohmischung aus Bisphenol und dem Phenol bei einer Temperatur oberhalb dem Siedepunkt des zugegebenen, flüchtigen, flüssigen Verdünnungsmittels; und
 - (b) kochen lassen des flüchtigen, flüssigen Verdünnungsmittels in dem Verfahren unter Abkühlung der resultierenden Mischung auf eine Temperatur, bei welcher sich die Adduktkristalle bilden.
2. Ein Verfahren nach Anspruch 1, in welchem das inerte, flüchtige, flüssige Kohlenwasserstoffverdünnungsmittel ein aliphatischer Kohlenwasserstoff bis 4 bis 6 Kohlenstoffatomen ist.
3. Ein Verfahren nach Anspruch 2, in welchem weniger als 1 Gewichtsprozent Wasser in der resultierenden Mischung vorliegen.
4. Ein Verfahren nach Anspruch 3, in welchem das inerte, flüchtige, flüssige Kohlenwasserstoffverdün-



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Example 2

Experiments similar to those described in Example 1 were conducted utilizing water and pentane.

The function of pentane in the above experiments was primarily to remove heat of adduct crystallization by vaporization instead of by use of direct contact with an external surface cooling means. Pentane also acts as an inert diluent (due to limited solubility in phenol) and lowers the cloud point of the crystallizing mixture by approximately 8 °C in the relative absence of water. The end crystallization temperatures are lowered proportionately and adduct recovery remains about the same as in the previous example.

Claims

1. A process for the preparation of crystals of an adduct of a bisphenol with a phenol which comprises:
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1. Ein Verfahren zur Herstellung von Kristallen eines Addukts eines Bisphenols mit einem Phenol, umfassend:
 - (a) das Zugabe von 8 bis 25 Gewichtsprozent eines inerten, flüchtigen, flüssigen, aliphatischen Kohlenwasserstoffverdünnungsmittels und 0 bis 1,5 Gewichtsprozent Wasser zu einer Rohmischung aus Bisphenol und dem Phenol bei einer Temperatur oberhalb dem Siedepunkt des zugegebenen, flüchtigen, flüssigen Verdünnungsmittels; und
 - (b) kochen lassen des flüchtigen, flüssigen Verdünnungsmittels in dem Verfahren unter Abkühlung der resultierenden Mischung auf eine Temperatur, bei welcher sich die Addukt-kristalle bilden.
2. Ein Verfahren nach Anspruch 1, in welchem das inerte, flüchtige, flüssige Kohlenwasserstoffverdünnungsmittel ein aliphatischer Kohlenwasserstoff bis 4 bis 6 Kohlenstoffatomen ist.
3. Ein Verfahren nach Anspruch 2, in welchem weniger als 1 Gewichtsprozent Wasser in der resultierenden Mischung vorliegen.
4. Ein Verfahren nach Anspruch 3, in welchem das inerte, flüchtige, flüssige Kohlenwasserstoffverdün-



nungsmittel Butan oder Hexan ist.

5. Ein Verfahren nach Anspruch 3, in welchem das inerte, flüchtige, flüssige Kohlenwasserstoffverdünungsmittel Pentan ist.
- 5 6. Ein Verfahren nach den Ansprüchen 1 bis 5, in welchem 0,25 bis 1,5 Gewichtsprozent Wasser, bezogen auf die Mutterlauge, vorliegen.
7. Ein Verfahren nach Anspruch 6, in welchem 0,3 bis 1,0 Gewichtsprozent Wasser vorliegen.
- 10 8. Ein Verfahren nach den Ansprüchen 1 bis 7, in welchem das Bisphenol Bisphenol A ist.

Revendications

- 15 1. Procédé de préparation de cristaux d'un produit d'addition de bisphénol avec un phénol, dans lequel :
(a) on ajoute 8 à 25% en poids d'un diluant hydrocarboné aliphatique liquide volatil inerte et de 0 à 1,5% en poids d'eau à mélange brut du bisphénol et du phénol à une température supérieure à la température d'ébullition du diluant liquide volatil ajouté ; et
20 (b) on laisse bouillir le diluant liquide volatil dans le procédé, refroidissant ainsi le mélange résultant à une température à laquelle les cristaux du produit d'addition se forment.
2. Procédé selon la revendication 1, dans lequel le diluant hydrocarboné liquide volatil inerte est un hydrocarbure aliphatique contenant de 4 à 6 atomes de carbone.
- 25 3. Procédé selon la revendication 2, dans lequel moins de 1% en poids d'eau est présent dans le mélange résultant.
4. Procédé selon la revendication 3, dans lequel le diluant hydrocarboné liquide volatil inerte est le butane ou l'hexane.
- 30 5. Procédé selon la revendication 3, dans lequel le diluant hydrocarboné liquide volatil inerte est le pentane.
6. Procédé selon les revendications 1 à 5, dans lequel de 0,25 à 1,5% en poids d'eau sont présents sur la base de la liqueur mère.
- 35 7. Procédé selon la revendication 6, dans lequel 0,3 à 1,0% en poids d'eau sont présents.
8. Procédé selon les revendications 1 à 7, dans lequel le bisphénol est le bisphénol A.