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PROCESS FOR PRODUCING BISPHENOL A

5 Technical Field:

This invention relates to an economical process for the production of high grade bisphenol A which is excellent in color hue and which is thermally stable and is not colored at a high temperature.

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Background Art:

One known method of producing bisphenol A (hereinafter referred to as BPA) includes a step of introducing crude BPA, which contains impurities such as reaction by-products, into a crystallizer to form crystals of an adduct of BPA with phenol and a mother liquor. The crystals separated from a mother liquor are introduced into a dephenolation step to remove phenol and to yield high purity BPA. Most of the mother liquor is recycled to a reaction zone while a portion thereof is purged and treated to obtain a purified mother liquor and a residual tar. The purified mother liquor is recycled to the reaction zone.

The crude BPA also contains an acid contaminant which causes decomposition of BPA and production of phenol and isopropenyl phenol during distillation, crystallization, and other steps. Thus, it is undesirable to let the acid contaminant to accumulate in the system. In the above process, the acid contaminant may be discharged from the system together with the tar. However, in order to maintain the concentration of the acid contaminant in the process line at an acceptable level, it is necessary to increase the purge flow rate of tar purge to exhaust the acid contaminant with process fluid containing phenol, impurities like 2,4'-BPA, etc. This

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operation causes a problem of an increase in BPA production costs.

Disclosure of the Invention:

5 The present invention has been made in view of the above problem and is aimed to provide an economical process which can reduce raw material phenol consumption without adversely affecting the grade of product BPA.

10 In accordance with the present invention there is provided a process for producing bisphenol A, comprising the steps of:

 (a) reacting a feed containing phenol and acetone in the presence of an acid catalyst to obtain a product stream containing bisphenol A, phenol and an acid
15 contaminant;

 (b) distilling said product stream to remove acetone and to obtain a bottom stream containing bisphenol A, phenol and an acid contaminant;

20 (c) crystallizing said bottom stream to obtain crystals of adduct of bisphenol A with phenol and a mother liquor containing an acid contaminant and phenol;

 (d) removing phenol from said crystals to yield bisphenol A;

25 (e) recycling a first portion of said mother liquor to step (a) as part of said feed;

 (f) treating a second, remainder portion of said mother liquor to purge a residual tar and to recover a purified liquor, the amount of said second portion being 0.5-5 parts by weight per 100 parts by weight of said
30 mother liquor;

 (g) recycling said purified liquor to step (a) as part of said feed; and

 (h) subjecting at least one of (i) at least part of said feed, (ii) at least part of said product stream and
35 (iii) at least part of said first portion of said mother

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liquor to a treatment for removing the acid contaminant contained therein, so that the concentration of the acid contaminant in said bottom stream to be supplied to step (c) is maintained within a range of 0.001-0.5 meq/L.

5 The present invention will be described in detail below with reference to the accompanying drawing, in which:

Fig. 1 is a flow sheet for a system suited for carrying out a process of producing BPA in accordance with
10 the present invention.

Referring to Fig. 1, designated as 1 is a reactor to which a feed containing raw materials (mixture of phenol and acetone) from a line 11 is fed through lines 13 and 15. In the reactor 1, acetone and phenol are reacted in the
15 presence of a strong acid catalyst such as a sulfonic acid-type cation exchange resin. The reaction is generally carried out at a temperature of 45-95°C, preferably 55-85°C. The reaction pressure has little influence upon the BPA producing reaction and is not
20 specifically limited. When the reactor 1 is a fixed bed system, the reaction pressure is preferably in the range of 0.05-0.5 MPa from the standpoint of required mechanical strength of the reactor or avoidance of catalyst crush.

The sulfonic acid-type cation exchange resin is
25 preferably in the form of a gel and is partially modified with a sulfur-containing compound, preferably a compound having a mercapto group and a tertiary nitrogen-containing group, such as mercaptoalkylpyridine or mercaptoalkylamine. Examples of the sulfur-containing compounds include 2-
30 mercaptoethylamine and 2,2-dimethylthiazolidine. The modification of the cation exchange resin may be performed by reacting the resin with a sulfur-containing compound in water or in an organic solvent such that a part of, generally 3-30 % of, preferably 5-15 % of, the sulfonic
35 acid groups are modified with the sulfur-containing

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compound.

The catalyst is preferably in the form of particles and packed in a cylindrical reactor. The average particle diameter of the catalyst particles is preferably 0.2-2.0
5 mm, more preferably 0.4-1.5 mm with the uniformity of particle diameter distribution being in the range of 1.0-1.4, preferably 1.0-1.3. The average particle diameter herein and the uniformity of particle diameter distribution are as measured in the state where the
10 catalyst particles are swollen with water. The uniformity of particle diameter distribution Z is defined by the formula:

$$Z = A/B$$

wherein A and B are the sizes of openings of sieves
15 through which 40 volume % and 90 % by volume of the catalyst particles remain unpassed, respectively.

The reaction mixture in the reactor 1 is discharged therefrom as a product stream through a line 17. The product stream which contains bisphenol A, phenol,
20 unreacted acetone, an acid contaminant or free acid derived from the acid catalyst, reaction by-products, etc. is fed through a line 20 to a distillation zone 2, such as a distillation tower and/or an evaporator, where a distillate containing water, unreacted acetone and part of
25 phenol is separated and discharged through a line 21. A bottom stream from the distillation zone 2 containing bisphenol A, phenol and an acid contaminant is fed through a line 22 to a crystallizing zone 3, where the bottom stream is cooled to form crystals of adduct of bisphenol A
30 with phenol. The crystals are separated from the mother liquor containing an acid contaminant and phenol and then sent to a next dephenolation step 8 through a line 23. Preferably, the crystallization is repeated two or more times.

35 In one preferred embodiment, the crystallization in

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the crystallizing zone 3 is performed in a series of first and second crystallization stages and wherein crystals obtained in the first crystallization stage are dissolved in phenol, suitably a mother liquor separated from the
5 second crystallization stage, the resulting solution being subjected to crystallization in the second crystallization stage.

The first crystallization stage is preferably carried out using a series of two, first and second
10 crystallizers in such a manner that the bottom stream from the distillation zone is cooled to form relatively large crystals (pure seed crystals) of the adduct crystals having less than 30 % by weight of a content of fine crystals with a diameter of 100 μm or less. The seed
15 crystals-containing slurry in the first crystallizer is fed to the second crystallizer and cooled at a temperature lower than the temperature of the first crystallizer to grow the seed crystals and to form adduct crystals having less than 30 % by weight of a content of fine crystals
20 with a diameter of 100 μm or less.

The crystals formed in the second crystallizer are separated from the mother liquor and are dissolved with phenol again. The solution is crystallized in the second crystallization stage which is also preferably carried out
25 using a series of two, third and fourth crystallizers. Thus, the solution is fed to the third crystallizer and cooled to form relatively large crystals (pure seed crystals) of the adduct having less than 30 % by weight of a content of fine crystals with a diameter of 100 μm or
30 less. The seed crystals-containing slurry in the third crystallizer is fed to the fourth crystallizer and cooled at a temperature lower than the third crystallizer temperature to grow the seed crystals and to form crystals having less than 30 % by weight of a content of fine
35 crystals with a diameter of 100 μm or less. The crystals

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formed in the fourth crystallizer are separated from the mother liquor, melted by heat and sent to a next dephenolation step. The mother liquor obtained in the second crystallization stage is preferably used to
5 dissolve the adduct crystals obtained in the first crystallization stage.

The melted crystals of the adduct of bisphenol A with phenol obtained in the crystallizing zone 3 are sent to the dephenolation step 8, where the phenol is removed
10 from said crystals to yield bisphenol A which is recovered through a line 32. The dephenolation may be carried out by any suitable known method.

In one preferred embodiment according to the present invention, the dephenolation is performed by melting the
15 crystals to form a melt containing bisphenol A and phenol, the resulting melt being heated to evaporate the phenol. If desired, the evaporation may be followed by stripping, for example, steam stripping.

It is preferred that, before the evaporation, the
20 melt be contacted with a cation donating solid to neutralize a strong acid contained in the melt with the cation donating solid. By this treatment with the cation donating solid, decomposition of bisphenol A during the heating of the melt can be effectively prevented and a
25 high purity high grade bisphenol A can be recovered with a high yield. As the cation donating solid, a glass fiber may be suitably used.

The mother liquor obtained in the crystallizing zone 3 is generally composed of 8-12 % by weight of bisphenol A,
30 75-90 % by weight of phenol and 5-15 % by weight of impurities such as acid contaminant, polyphenols such as trisphenol and coumarone compounds. Most of the mother liquor is recycled through lines 24, 31, 12, 13 and 16 to the reactor 1 as part of the feed. Another, remainder
35 portion of the mother liquor, which is 0.5-5 parts by

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weight per 100 parts by weight of the mother liquor, is fed to a purge recovering zone 4 through a line 25. In the purge recovering zone 4, the liquid is treated to purge tarry compounds and to recover a purified mother liquor. Acid compounds are also separated from the mother liquor. When the amount of the mother liquor fed to the purge recovering zone 4 is less than 0.5 part or less, impurities such as high boiling matters and acid contaminants are built up in the system to cause a reduction of the grade of BPA. Too large an amount of the mother liquor fed to the purge recovering zone 4 in excess of 5 parts by weight per 100 parts by weight of the mother liquor increases the raw material consumption and is economically disadvantageous because phenol loss increases.

Preferably, the purge recovering zone 4 includes a phenol distillation tower, a reactor provided with an evaporator operated under vacuum conditions and a strong acid-type ion exchange resin-containing tower. In the purge recovering zone 4, the mother liquor stream 25 is first fed to the distillation tower to recover a phenol as distillate. The bottom stream, concentrated mother liquor, is introduced into the reactor with added basic catalyst, where bisphenol, trisphenol and other polyphenols contained in the bottom stream are thermally cracked into isopropenylphenol and phenol by the catalyst, while the impurities such as chromans compounds are polycondensed to form high boiling matters, tar.

The recovered vapors of isopropenyl phenol and phenol from the reactor are introduced into the condenser where the vapors are contacted with the distillate from the distillation tower and condensed. The condensed stream is then fed to the strong acid-type ion exchange resin-containing tower so that bisphenol A is formed as a result of the reaction of phenol with isopropenyl phenol. The effluent from the tower represents the purified liquor

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obtained from the purge recovering zone 4 and is recycled to the reactor 1 through lines 27, 12, 13 and 16. The high boiling matters obtained in the reactor is discharged as residual tar through a line 26.

5 If desired, the tar from the line 26 may be used as a fuel oil by being mixed and diluted with an ether by-products oil including aromatic ether obtained from a phenol production process. The tar at 180-230°C is fed to a mixing zone to which the dilutant by-products oil
10 including aromatic ether at 60-170°C is fed for mixing with the tar. The mixing ratio of the dilutant to the tar is 0.1:1 to 2:1. The mixture discharged from the mixing zone is cooled so that the temperature of the cooled mixture is 80-150°C. A portion of the cooled mixture is
15 recycled to the mixing zone, with the remainder portion being recovered as the fuel oil.

 In the present invention, it is important that the concentration of the acid contaminant in the stream 22 to be supplied to the crystallizing zone 3 should be
20 maintained within a range of 0.001-0.5 meq/L (milliequivalent/liter), preferably 0.001-0.10 meq/L, in order to obtain high grade crystals of adduct in the crystallizing zone 3. Such high grade crystals have actually no acid contaminant content in terms of the acid
25 content in a melt of the crystals. When the concentration of the acid contaminant in the stream 22 to be supplied to the crystallizing zone 3 exceeds 0.5 meq/L, part of the acid contaminant is included in the crystals of the adduct obtained in the crystallizing zone. As a result, in the
30 succeeding dephenolation step 8, the acid contaminant causes decomposition of BPA, resulting in an increase of phenol content in the BPA and coloring and degrading of the product BPA.

 Thus, in the present invention, at least one of
35 (i) at least part of the feed introduced to the reactor 1

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through the lines 13 and 16,

(ii) at least part of the product stream fed from the reactor 1 to the distillation zone 2 through the lines 17 and 20, and

5 (iii) at least part of the mother liquor which is recycled through the lines 24, 31, 12, 13 and 16 to the reactor 1 is subjected to a treatment for removing the acid contaminant contained therein, so that the concentration of the acid contaminant in the stream 22 to be supplied to
10 the crystallizing zone 3 is maintained within a range of 0.001-0.5 meq/L.

The lower limit of the acid contaminant concentration is 0.001 meq/L from the economical viewpoint, since a giant acid removing system is required in order to
15 reduce the concentration of the acid contaminant in the bottom stream to an extremely low level.

The acid contaminant may be removed by contacting the acid contaminant-containing fluid with an absorbent which scarcely elutes impurities. Examples of such
20 absorbents include activated carbon, alkaline inorganic oxides and anion exchange resins. The anion exchange resins are preferably used. While various kinds of anion exchange resins can be suitably used for the purpose of the present invention, the use of anion exchange resins
25 having weak basic anion exchanging groups such as primary, secondary or tertiary amines is preferred. Illustrative of suitable anion exchange resins are Amberlite (manufactured by Rohm and Haas Company), Dowex (manufactured by Dow Chemical Inc.) and Diaion
30 (manufactured by Mitsubishi Chemical Company).

In the illustrated embodiments, (i) a portion or all of the feed in the line 13 is introduced through a line 14 into an acid treatment zone 5 and fed to the reactor 1 through a line 15, (ii) a portion or all of the product
35 stream in the line 17 is introduced through a line 18

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into an acid treatment zone 6 and fed to the distilling zone 2 through a line 19, and (iii) a portion or all of the mother liquor in the line 28 is introduced through a line 29 into an acid treatment zone 7 and fed to the reactor 1 through a line 31. However, one or two of the above treatment zones 5, 6 and 7 can be omitted, if desired. It is preferred that the acid contaminant be removed only in the acid treatment zone 7 from the economical standpoint. Because the concentration of the acid contaminant per unit volume of the stream in the line 28 is higher than that in the line 13, 14, 17 and 18, the acid removal in the zone 7 is more effective and efficient than in the zone 5 or 6.

The amount of the stream to be treated in each of the acid removing zones 5-7 may be suitably determined according to the concentration of the acid contaminant in the stream to be treated.

In the present invention, it is no longer necessary that the flow rate of the stream 25 to purge recovery zone 4 should be increased to remove acid contaminant, since the acid contaminants in the process stream are removed in at least one of the acid removing zones 5-7. The treatment in the purge recovery zone 4 may be carried out only for the purpose of reducing impurities other than acid contaminants. Thus, even when the amount of the purge is reduced, the quality of the crystals of the adduct obtained in the crystallization zone 3 is not adversely affected. As a consequence, the amount of the tars discharged through the line 26 can be reduced.

Thus, it is possible to produce high grade crystalline adduct of BPA with phenol free of an acid contaminant or free acid and, hence, to produce high grade BPA free of coloring bodies, according to the process of the present invention. The system for treating the purge can be made compact and the amount of tars discharged

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therefrom is small, since the amount of the purge from the process line is small. Therefore, it is possible to reduce the amount of acetone and phenol supplied as raw materials can be reduced so that the production costs of BPA can be reduced. Further, since the acid treatment in the present invention is performed such that the concentration of the acid contaminant in the bottom stream to be supplied to the crystallizing zone is maintained within a range of 0.001-0.5 meq/L, the operation load in the acid removal step can be reduced and the amount of the absorbent in the acid treatment can be reduced. Thus, the acid can be removed with reduced costs.

The following examples will further illustrate the present invention. Percentage is by weight.

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Example 1

Using the apparatus shown by the flow sheet of Fig. 1, BPA was produced. The acid removing steps in 5 and 6 were omitted and the acid treatment was carried out only in the step 7. In the crystallizing zone 3, crystals of the adduct were washed with 23.2 kg/h of pure phenol. The flow rates, conditions and analytical data were as shown below.

25 Reactor 1:

Reaction temperature: 60°C

Reaction pressure: 0.3 MPa

Catalyst: Sulfonic acid-type cation exchange resin

(manufactured by Rohm & Haas Company; Amberlite 118-H, average particle diameter: 0.54 mm, uniformity off particle diameter distribution: 1.46) was sieved to obtain a sieved product having an average particle diameter of 0.69 mm and uniformity of particle diameter distribution of 1.17. The sieved product was treated so that 10 % of the sulfonic

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groups thereof were modified with 2-mercaptoamine to obtain the catalyst.

Product Stream in Line 17:

Flow rate: 116.7 kg/h

5 Composition

BPA: 18.8 %

Phenol: 73.6 %

Water: 1.0 %

Acetone: 0.8 %

10 Free acid: 0.086 meq/L

Other impurities: 5.8 %

Distillate in Line 21:

Flow rate: 17.8 kg/h

Composition

15 Water: 7 %

Acetone: 6 %

Phenol: 86 %

Others: 1 %

Bottom Stream in Line 22:

20 Flow rate: 98.9 kg/h

Composition

BPA: 22 %

Phenol: 74 %

Free acid: 0.101 meq/L

25 Other impurities: 4 %

Crystals of Adduct in Line 23:

Flow rate: 22.1 kg/h

Free acid: below measurable limit
(≤ 0.001 meq/L)

30 Mother Liquor in Line 24:

Flow rate: 100 kg/h

Composition

BPA: 8 %

Phenol: 86 %

35 Free acid: 0.1 meq/L

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Other impurities: 6 %

Purge in Line 25:

Flow rate: 3 kg/h (3 parts by weight per 100
parts by weight of the mother
liquor in line 24)

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Purge Recovery Step 4:

Reactor/Vacuum Condenser:

Bottom temperature: 250°C

Pressure: 0.02 MPa

10 Strong acid-type ion exchange resin tower

Temperature: 53°C

Pressure: 0.1 MPa

Tars in Line 26:

Flow rate: 0.2 kg/h

15 Purified Liquor in Line 27:

Flow rate: 2.8 kg/h

Composition

BPA: 8 %

Phenol: 89.5 %

20 Free acid: below measurable limit
(≤ 0.001 meq/L)

Other impurities: 2.5 %

Mother Liquor in Line 28:

Flow rate: 97 kg/h

25 Mother Liquor in Line 29:

Flow rate: 7.0 kg/h

Free acid: 0.1 meq/L

Acid Removal Step 7:

Absorbent: Anion exchange resin having secondary amines
(Amberlite manufactured by Rohm & Haas
Company)

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Temperature: 50°C

Treated Liquor in Line 30:

Free acid: below measurable limit
(≤ 0.001 meq/L)

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Feed in Line 16:

Flow rate: 116.7 kg/h

Free acid: 0.078 meq/L

BPA from Line 32:

- 5 Flow rate: 13.0 kg/h
Free acid: below measurable limit
(≤ 0.001 meq/L)
Phenol: below 15 ppm by weight

10 Comparative Example 1

Example 1 was repeated in the same manner as described except that the acid removal treatment at zone 7 was not carried out. Thus, the mother liquor in the line 28 was directly passed to the line 31 and fed to the
15 reactor 1. In this case, the concentration of the free acid (acid contaminant) in the bottom stream in the line 22 was higher than 0.101 meq/L. In order to maintain the free acid content in 0.101 meq/L in the line 22, it was
20 necessary to increase the amount of the mother liquor purged through the line 25 to 10 kg/h. As a result, the amount of tars discharged through the line 26 increased to 0.7 kg/h. The BPA production cost was thus higher than that in Example 1.

25 Comparative Example 2

Example 1 was repeated in the same manner as described except that the acid removal treatment at zone 7 was not carried out and that the amount of the mother liquor purged through the line 25 was reduced to 0.5 kg/h.
30 In this case the amount of tars discharged through the line 26 was 0.05 kg/h. However, the concentration of the free acid in the bottom stream in the line 22 increased above 2.0 meq/L, so that BPA decomposed in dephenolation stage 8. The BPA product recovered through the line 32
35 had a phenol concentration of 100-1000 ppm by weight.

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CLAIMS

1. A process for producing bisphenol A, comprising the steps of:

- 5 (a) reacting a feed containing phenol and acetone in the presence of an acid catalyst to obtain a product stream containing bisphenol A, phenol and an acid contaminant;
- (b) distilling said product stream to remove acetone
10 and to obtain a bottom stream containing bisphenol A, phenol and an acid contaminant;
- (c) crystallizing said bottom stream to obtain crystals of adduct of bisphenol A with phenol and a mother liquor containing an acid contaminant and phenol;
- 15 (d) removing phenol from said crystals to yield bisphenol A;
- (e) recycling a first portion of said mother liquor to step (a) as part of said feed;
- (f) treating a second, remainder portion of said
20 mother liquor to purge a residual tar and to recover a purified liquor, the amount of said second portion being 0.5-5 parts by weight per 100 parts by weight of said mother liquor;
- (g) recycling said purified liquor to step (a) as
25 part of said feed; and
- (h) treating at least one of (i) at least part of said feed, (ii) at least part of said product stream and (iii) at least part of said first portion of said mother liquor to remove the acid contaminant contained therein,
30 so that the concentration of the acid contaminant in said stream to be supplied to step (c) is maintained within a range of 0.001-0.5 meq/L.

2. A process as claimed in claim 1, wherein step (h) is
35 carried out by contact with an adsorbent.

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3. A process as claimed in claim 2, wherein said adsorbent is a basic cation exchange resin.

5 4. A process as claimed in claim 1, wherein step (c) comprises a series of first and second crystallization stages and wherein crystals obtained in the first crystallization stage are dissolved in a mother liquor obtained in the second crystallization stage and the
10 resulting solution is subjected to crystallization in the second crystallization stage.

5. A process as claimed in claim 1, wherein step (d) comprises melting said crystals to form a melt containing
15 bisphenol A and phenol, and heating said melt to evaporate the phenol.

6. A process as claimed in claim 5, wherein, before said heating, said melt is contacted with a cation donating
20 solid to neutralize a strong acid contained in said melt with said solid.

7. A process as claimed in claim 6, wherein said cation donating solid is a glass fiber.
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