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10 **DESCALING OF BISPHENOL-A REACTOR USING WATER****Background of the Invention****Field of the Invention**

The invention relates to a batch, semi-continuous or continuous process for the manufacture of bisphenol-A.

15 **Brief Description of Related Art**

The dihydric phenol 2,2 bis(p-hydroxyphenyl) propane (commonly referred to as "bisphenol-A", "BPA" or "pp-BPA") is commercially prepared by condensing 2 moles of phenol with a mole of acetone in the presence of an acid catalyst. The phenol is present in the reaction in a molar excess of the
20 stoichiometric requirement. During the condensation, a number of by-products such as isomeric forms of the BPA are formed which are considered contaminants of the desired product, BPA. These contaminants are carried in the product stream from the condensation reaction zone, referred to as the condensation
25 product effluent, along with water, unreacted phenol, possibly unreacted acetone and possibly trace quantities of acidic materials derived from the catalyst. Currently, the purification of the desired product BPA is a costly and multi-step procedure.

There are two commercially important processes
30 for the synthesis of BPA currently in use. One process is sometimes called the "HCL" process, in reference to the acidic catalyst employed (hydrogen chloride).

The second synthesis involves the use of an active ion exchange catalyst
35 and is sometimes called the "IER" process. Both synthesis involve passing phenol, acetone and recycled by-products through a reactor containing an acid

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catalyst followed by a BPA purification scheme.

The "IER process" can be done in one of two ways; first, until essentially complete acetone depletion; second, and most desirable, is "partial acetone conversion". This technology is described in U.S. Patent 5,315,042 . The BPA reaction can be optionally promoted by the presence of a free mercaptan such as 3-mercaptopropionic acid, or use a promoter which is chemically or covalently bonded to the IER resin, or use no promoter. These resins are generally well known compositions as are methods of their preparation; see for example the preparative procedures described in U.S. Patent 3,037,052 .

The HCl process reaction effluent contains phenol, BPA, a 1:1 adduct of BPA and phenol, isomeric by-products of BPA and impurities along with the promoter (when present) and possibly unreacted acetone. This effluent, also sometimes referred to as the HCl process reaction effluent, may be fed to a stripping operation which removes the water of reaction, HCl, phenol and possibly residual acetone and/or promoter.

Representative of more detailed descriptions of the above processes for condensing phenol with acetone to obtain BPA are those found in the U.S. Patents 4,346,247; 4,396,728; 4,400,555; 4,424,283; 4,584,416; 4,766,254 and 4,847,433. The factor shared by all of these known methods and processes is the need to purify and recover the product BPA. This can be done by the 1:1 BPA/Phenol adduct crystallization (U.S. Pat. No. 5,210,329) as the desired BPA forms a 1:1 adduct with excess phenol.

EP-A 0 332 877 issued to Mitsui Toatsu Chemicals(JP) describes a process for producing high-purity bisphenol-A which comprises reacting phenol with acetone in the presence of hydrochloric acid as the catalyst to obtain a product mixture, removing the hydrochloric acid from the product mixture, thereby yielding a liquid mixture, adding water to the liquid mixture, evaporating a water-phenol mixture from the liquid mixture under reduced pressure, thereby cooling the liquid mixture and crystallizing out the adduct of bisphenol-A with phenol, and finally recovering bisphenol-A from the adduct.

JP-A 58135832 issued to Mitsui Toatsu Chemical Inc. describes a process for continuous crystallization of bisphenol-A in high purity from a solution of bisphenol-A in phenol, by cooling the solution under a specific pressure while adding a proper amount of water to the system.

US-A 4 209 646 issued to Rhone-Poulenc Industries (Paris, FR) describes a process for crystallizing an adduct of diphenyl propane and phenol to obtain purified

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diphenyl propane.

The present invention is a modified process for producing purified BPA in a fully integrated, batch, semi-continuous or continuous commercial process beginning with the condensation reaction product.

Summary of the Invention

The invention comprises, a process for the batch, semi-continuous, or continuous manufacture of bisphenol-A by condensing phenol with acetone, comprising:

forming a reaction mixture comprising acetone, a stoichiometric excess of the phenol and a catalytic amount of an acid catalyst in a reaction zone and at a temperature effective to produce bisphenol-A and a 1:1 bisphenol-A/phenol adduct;

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removing an effluent from the first reaction zone, wherein the effluent comprises unreacted phenol, unreacted acetone, and the 1:1:bisphenol-A/phenol/adduct;

precipitating crystals of the adduct from the reaction mixture, the effluent, or a mixture thereof, wherein a portion of the crystals become affixed to a surface of the reactor, and;

removing at least a portion of the precipitated crystals from the surface by adding water to the reaction mixture, the effluent, or a combination thereof, in an amount of 1-40% by weight of the reaction mixture, the effluent, or the combination thereof, and heating the reaction mixture, the effluent, or a combination thereof to a temperature in the range of from 40°C to 95°C.

Brief Description of the Drawing

The accompanying drawing is a block diagram showing an embodiment of the process of the invention.

Detailed Description of a Preferred Embodiment of the Invention

The commercially important processes for preparing BPA comprise condensation of 2 moles of phenol with a mole of acetone in the presence of an acid catalyst and a stoichiometric excess of the phenol reactant; see for example the U.S. Patents referred to above in the Brief Description of the Related Art. As shown in the accompanying drawing, to illustrate an embodiment process of the present invention, this reaction is the starting point of the present process which advantageously is conducted in a semi-continuous or continuous manner. In other words, the reactant phenol and acetone are fed continuously in measured proportions to the reaction zone and the product of condensation is continuously carried away from the reactor zone. Any of the previously described reaction conditions and catalysts can be employed to obtain the reaction zone effluent for continued handling according to the process of the invention.

Preferred is the condensation procedure of U.S. Pat. No. 5,315,042,

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carried out semi-continuously.

As depicted in the accompanying drawing, the condensation and crystallization of BPA-Phenol adduct is carried out conventionally in a reaction zone (12). The reaction effluent containing crude BPA, phenol, isomers of BPA, impurities, water, a 1:1 adduct of phenol and bisphenol-A, other reaction by-products and possibly acetone and promoter is conventionally carried to a multiple stage recovery of acid, water and phenol followed by further purification steps.

The molten pure BPA product from the recovery unit can be recovered in a variety of forms including "flakes" by solidifying the melt on a cooled rotating drum, or as, "prills" from a prilling operation. In the reaction/crystallization unit or units, the precipitated crystals deposit on the cooler surfaces of the unit to "build-up" a deposit. When this build-up of crystals becomes problematic with regard to cooling efficiency or scales of crystals coming loose, the build-up can be removed by using the following procedure:

- 1 Stop the acetone feed and empty (fully or partially) the continuous or batch reactor/crystallizer.
- 2 Fill the reactor up with phenol, dissolve the build-up by heating the phenol/reaction mixture to 50⁰ -90⁰C.
- 3 Start the acetone feed gently while applying HCl pressure.

These procedures interrupt the continuity of the continuous feed to the recovery/production of BPA and, accordingly, are disadvantageous.

In a continuous or semi-continuous manufacture of bisphenol, with continuous flow of product effluent from the reactor, descaling of the reaction vessels can be done with minimal/no interruption of feed of reagent to the continuous reactor by adjusting the water content & temperature of the continuous and batch reactors so as to contain 5 to 40 weight percent of water at 50 –95 degC. This can be accomplished by:

1. Adding water, preferably 1-40 wt % water, dosed as pure water or more preferably dosed as 1.3 to 63 wt % HCl (as a 33% solution) or a combination of water and HCl solution, to the continuous or batch reactors. During this step, it is not necessary to stop the acetone addition (if the reactor set up is continuous) or to reduce the HCl pressure.
2. Heat the reactor contents to 55⁰ -95⁰C, via external heat, via heat of reaction or via heat of dissolution of the acid in the reaction medium or a

combination thereof. Again, during this step, it is not necessary to stop the acetone addition (if the reactor set up is continuous) or to reduce the HCl pressure. This step is optional because, if enough water is added, the BPA phenol adduct will dissolve without extra heating.

- 5 3. If heating was applied in Step 2, cool down reactor contents gently, while continuing "normal" operation. When normal operation is resumed, the water content in the reactors will decrease to the normal level smoothly and automatically crystallization will occur and operation will become normal.

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Surprisingly, the large amount of water (of HCl) does not affect the acetone conversion or BPA finished product quality.

- 15 The results are shown in the Table, below compared to the prior art procedure of interrupting the condensation reaction to flush the reactors with hot phenol.

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	Dissolving 30% BPA crystals with Phenol (60%) and water (10%)	Dissolving BPA crystals with Phenol	Dissolving 20% BPA crystals with Phenol (72.5%), Acetone (2.5%) and Water (5%) in continuous reactor
Time needed for de-scaling operation 0-5 tons	0.5 hours	12 hours	0.5 hours
Production loss	0-2 tons	35 tons	0-5 tons
Minimum temperature required to dissolve 30% BPA	70 ⁰ C	82 ⁰ C	60 ⁰ C
Quantity of phenol (or water) needed to dissolve all BPA	5-10 tons	25 tons phenol	2.25 tons water
Acetone conversion after 6 hours	100%	100%	100%
% o/p BPA in F.P. when cooling reactor down to 50 ⁰ C	2500ppm	1850ppm	1850ppm

The concept is applicable to other commercial BPA processes employing multi-stage purification systems, such as adduct and melt crystallization(as described, for example, in U.S. Patent 5,243,093).

CLAIMS

1. A process for the batch, semi-continuous, or continuous manufacture of bisphenol-A by condensing phenol with acetone, comprising
forming a reaction mixture comprising acetone, a stoichiometric excess of the phenol and a catalytic amount of an acid catalyst in a reaction zone and at a temperature effective to produce bisphenol A and a 1:1 bisphenol-A/phenol adduct;
removing an effluent from the reaction zone, wherein the effluent comprises unreacted phenol, unreacted acetone, and the 1:1 bisphenol-A/phenol adduct;
precipitating crystals of the adduct from the reaction mixture, the effluent, or a mixture thereof, wherein a portion of the crystals become affixed to a surface of the reactor; and
removing at least a portion of the precipitated crystals from the surface by adding water to the reaction mixture, the effluent, or a combination thereof, in an amount of 1-40% by weight of the reaction mixture, the effluent, or the combination thereof, and heating the reaction mixture, the effluent, or a combination thereof to a temperature in the range of from 40⁰C to 95⁰C.

2. The method of claim 1, wherein the water further comprises HCl in an amount of 1.3 to 63% by weight of the reaction mixture, the effluent, or the combination thereof.

3. The method of claim 1, wherein the water comprises HCl in an amount of 33% by weight of the water.

4. The method of claim 1, wherein the reaction mixture and added water, the effluent and added water, or the combination of reaction

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mixture and effluent and added water is heated to a temperature in the range from 40 to 95⁰C.

5. The method of claim 4, wherein the reaction mixture and added water, the effluent and added water, or the combination of reaction mixture and effluent with added water is heated to a temperature in the range from 50 to 95⁰C.

6. The method of claim 4, wherein the reaction mixture and added water, the effluent and added water, or the combination of reaction mixture and effluent with added water is heated to a temperature in the range from 55 to 95⁰C.

7. The method of claim 1, wherein the heating or maintaining is by the heat of the reaction, the heat of dissolution of the acid, by application of external heat, or by a combination thereof.

8. The method of claim 1, wherein the process is a semi-continuous or continuous process employing a continuous or semi-continuous feed of acetone, phenol, or a combination thereof, and wherein removing of the crystals is done with no interruption of the continuous or semi-continuous feed.

9. The method of claim 1, further comprising cooling the heated reaction mixture, effluent, or combination thereof after the crystals have been dissolved.