

Improved Method To Defoul Bisphenol-Phenol
Adduct Fouled Crystallizer Coolers

Background of the Invention

Field of the Invention

5 The invention relates to processes for the
synthesis of dihydric phenols and more particularly
to an improved process for recovering bisphenol-A.

Brief Description of Related Art

10 The dihydric phenol 2,2 bis(p-hydroxyphenyl)
propane (commonly referred to as "bisphenol-A") 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 a molar
15 excess of the stoichiometric requirement. During
the condensation, a number of by-products are
formed which are contaminants of the desired
product, bisphenol-A. These contaminants, carried
in the product stream from the condensation
20 reaction zone, include water, trace quantities of
acidic materials derived from the catalyst,
unreacted phenol and acetone and a number of
isomers of bisphenol-A.

Conventionally, an early step in separating
the desired bisphenol-A from the product stream may
25 involve cooling the product stream to induce
crystallization and precipitation of the
bisphenol-A in the form of a 1:1 adduct with the
excess of phenol present. The crystallized adduct
is separated, washed, and the phenol removed by
30 distillation, extraction or steam stripping.

In commercial plants for the synthesis of
bisphenols, the production of the bisphenol-phenol
adducts and delivery to crystallization coolers is
generally continuous or semi-continuous. Over
35 periods of time, the coolers will foul with

precipitated adduct, reducing their efficiency. This fouling can occur every 4 to 8 weeks, requiring an interruption in their use for a procedure commonly referred to as "meltout". The
5 procedure comprises passing hot phenol through the cooler system to melt out the deposits of crude bisphenol, which occurs mainly in the coolers.

An alternate procedure for defouling the coolers comprises heating both the coolers and the
10 crystallizers with process solutions containing typically 5.0 to 26.0 percent bisphenol to remove the bisphenol deposits coating the inside of the coolers and the crystallizers. The cooling medium in the heat exchanger is also warmed during the
15 meltout.

The time elapsing between meltouts is dictated-in-part by the efficiency of a preceding meltout and, in part, by operating conditions of the process reaction (rate of product delivery,
20 etc.). The frequency of required meltouts affects, of course, the overall efficiency of a commercial process line and the ultimate cost of the desired bisphenol product.

Further, meltouts are at times not successful,
25 when measured by the "Delta T" factor (temperature difference between the process solution and the cooling medium) which increases as the cooler becomes more fouled with bisphenol-phenol adduct on heat-exchanging surfaces.

30 We have now discovered that the efficiency of defouling coolers and crystallizers with hot phenol is improved substantially when the phenol contains a bisphenol solubilizing proportion of water. Fewer meltouts are required in a given time period,

requiring fewer interruptions of continuous and semi-continuous synthesis of the desired bisphenol.

Water has previously been added to the bisphenol-phenol adduct of crystallization to improve adduct purity. However, the process as described in U.S. Patent 4,950,806 (Imuro et al., 1990) requires a lower operating temperature due to the increased solubility of BPA. Other patents relating to water addition to adduct crystallization include U.S. 4,209,646 (Gac et al., 1980) describes BPA adduct crystallization with 2 to 20% water evaporative cooling. Japanese 83-135832 (Mitsui Toats 8/12/83) describes water addition to add crystals to control solution density and crystals. Japanese Patent JPO7069951-A recently issued to Idemitsu Petrochemical and Tsukishima Kikai Co. describes the use of phenol mixtures containing 1-20% water to reduce solids build-up in evaporative crystallization pipe through which the vaporized components pass. (Note that evaporative cooling involves the use of a vacuum and removal of water's heat of evaporation to cool and crystallize. In contrast, the present inventors use a separate cooling medium and shell and tube heat exchanger system to cool the process solutions.

Summary of the Invention

The invention comprises an improved method of defouling a cooling and crystallization surface, fouled upon crystallization of a 1:1 adduct of phenol and bisphenol-A thereon, which comprises: dissolving the adduct adhering on the surface with phenol containing from 3 to 40 weight percent of water.

Brief Description of the Drawings

Figure 1 is a block diagram representing a preferred embodiment of the invention.

Figure 2 is a graphical representation of the data obtained from a series of experiments to determine the solubility of BPA in solution of water in phenol.

Detailed Description of the Preferred Embodiment of the Invention

As mentioned above, commercial processes are known for the production of bisphenols by condensation of phenols with ketones, the initial crude product being a 1:1 adduct of the phenol with bisphenol. In an initial separation/purification the adduct is crystallized from the product stream of the condensation. Representative of many literature descriptions are those found, for example, in the U.S. Patent 4,051,079 (Melby) U.S. 4,950,806 (Imuro et al.); and 5,243,093 (Kissinger et al.), all incorporated herein by reference thereto. The majority of commercial processes are designed for continuous production, the adduct being present in the product stream flowing from the condensation reaction zone.

With reference to the accompanying drawing of a block diagram showing a portion of the commercial production of bisphenol, a molar excess of phenol is delivered to a reaction zone 12 with a ketone such as acetone. The condensation of the two reactants occurs continuously in reaction zone 12.

The reaction temperature in the reactor zone 12 may vary from 40° C. to 95° C. with reaction temperatures in the range of from 55° C. to 90° C. being preferred.

The reaction time in the reactor zone 12 may vary and depends on reaction temperature. For example, the liquid hour space velocity (LHSV) of the feed may vary between wide limits with
5 velocities in the range of from 0.2 to 40 liters feedstream/liter catalyst⁻¹/hour⁻¹.

The reaction zone 12 effluent is continuously withdrawn and fed to a system for separation of the product bisphenol-A. This effluent comprises
10 unreacted phenol, unreacted acetone, acid residues of the catalyst, water and isomers of bisphenol-A in admixture with the desired bisphenol-A. The isomers and by-products of interest are compounds wherein the hydroxy groups are not in the para
15 configuration relative to the isopropylidene group. It is this effluent which may provide a starting material for the method of the present invention. The effluent may be treated first by cooling to precipitate a crystalline 1:1 adduct of bisphenol-A
20 with phenol, and separating the solid adduct in a crystallizer 14. When the cooler surfaces in crystallizer 14 accumulate a deposit of the crystallized 1:1 adduct, crystallizer efficiency degrades. Ideally, the Delta-T of the cooling
25 surface is a less than about 4°C. The Delta-T is as mentioned above the temperature difference between the process solution and the cooling surface.

It cannot be stressed enough to maintain
30 Delta-T less than 4°. Having done this many times in a jacketed glass crystallizer, one can watch the nucleation, and vice versa, the erosion of build-up on the cool surface as the temperature is raised and lowered around the 4° Delta.

The following example and preparations describe the manner and process of making and using the invention and set forth the best mode contemplated by the inventor of carrying out the invention but are not to be construed as limiting the invention.

Lab Procedure

The following series of experiments were completed to determine the BPA solubility curves in phenol/water in the range of 5 to 40% water in phenol.

Add phenol and water as listed in the following table to a 250 ml flask.

TABLE

<u>experiment number</u>	<u>grams of water</u>	<u>grams of phenol</u>	<u>resulting % water in phenol</u>	<u>Grams of BPA dissolved per 100 grams of solution at 60°C</u>
1	5	95	5%	18
2	10	90	10%	31
3	20	80	20%	45
4	30	70	30%	85
5	40	60	40	>125

- 2) In each experiment add 5 grams of BPA, heat until homogeneous on a heated stir plate also with the aid of a heat gun as needed.
- 5 3) Cool with shaking, recording the exact temperature where cloudiness and crystallization begins.
- 10 4) Repeat steps 2 and 3 in each experiment adding between 5-20 grams of BPA each time. The data is collected using the total amount of BPA present in the flask.

The resulting BPA solubility curves (BPA vs temperature) show water/phenol mixtures will dissolve more BPA compared to pure phenol at higher temperatures; see the graphical representation of
15 Figure 2.

The use of phenol/water mixtures during meltout or intermittently between meltouts should reduce the time needed for a meltout or the frequency of required meltouts. There are several
20 options on how this invention can be practiced commercially, including but not limited to the following:

- 1) Crystallizer circulation can be stopped, process solutions can then be drained from the
25 cooler, and replaced with a hot phenol/water solution, and the shell side of the exchanger heated with steam to aid meltout of BPA adduct (and any by-products present). Agitation can be provided to increase efficiency.
- 30 2) The crystallizer circulation can be stopped, process solution drained from the cooler and replaced with Phenol with injection of steam into the phenol to increase the temperature and water content as well as provide some agitation. Steam
35 can also be added to the shell side of the cooler.

3) The crystallizer circulation can be stopped briefly and either phenol/water or phenol/steam or just steam can be injected directly into the process solution in the cooler (containing
5 Phenol/BPA/by-products and some water). The shell cooling medium can be turned off or warmed during this procedure. While this procedure briefly inhibits the crystallization process, carrying out this option intermittently to reduce buildup can
10 avoid actual shutdown of the line and significantly extend the time required between cooler meltouts. This eliminates downtime providing an increase in annualized production.

The added phenol/water or steam is compatible
15 with the present process. They will pass through the crystallizer and adduct filter into the mother liquor. From there the water can be removed by distillation (along with water formed in reaction). Any added phenol is also raw material which will be
20 converted to BPA upon recycle to reaction.

The examples have shown that water levels between 5 and 40% in phenol provide the increased BPA solubility relative to pure phenol.



WHAT IS CLAIMED IS:

1. An improved method of defouling a cooling and crystallization surface, fouled upon crystallization of a 1:1 adduct of phenol and bisphenol-A thereon, which comprises;

dissolving the adduct adhering on the surface with phenol containing from 5 to 40 weight percent of water.

2. The method of claim 1 wherein dissolving is carried out at a temperature of about 40 to 90°C.

3. The method of claim 1 wherein the crystallization is carried out in a continuous production of bisphenol.

4. In a method of continuously preparing a bisphenol, which comprises;

condensing a ketone with a phenol in the presence of a molar excess of the phenol whereby a reaction product is obtained containing a 1:1 adduct of the ketone and the phenol; and

separating the adduct from the reaction product by crystallization;

the improvement, which comprises;

- maintaining the Delta-T of the crystallizer at less than about 4°C.

5. The improved method of claim 4 wherein maintaining is carried out by dissolving adduct adhering to the crystallizer cooling surfaces.

6. The improved method of claim 5 wherein dissolution is in a phenol solution containing 5 to 40 percent (v/v) water.

7. The improved method of claim 6 wherein the phenol/water solution is at a temperature of about 40 to 90°C.

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8. The improved method of claim 6 wherein the phenol/water solution or steam is introduced into the crystallizer with the reaction product.

9. The improved method of claim 6 wherein the phenol/water solution or steam is introduced into the crystallizer sequentially following the reaction product.

10. The improved method of claim 4 wherein the bisphenol is bisphenol-A and the ketone is acetone.

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