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(54) **Process for the purification of 4,4'-dihydroxydiphenyl**

(57) A process for purifying 4,4'-dihydroxydiphenyl comprising contacting a solution of an alkali metal salt of 4,4'-dihydroxydiphenyl with activated carbon followed by removing the activated carbon from the solution and acidifying the solution with sufficient acid to convert essentially all of the 4,4'-dihydroxydiphenyl alkali metal salt to water insoluble 4,4'-dihydroxydiphenyl and a 4,4'-dihydroxydiphenyl product containing less than 0.45 weight percent of 4-monohydroxydiphenyl impurity.

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SPECIFICATION

Process for the purification of 4,4'-dihydroxydiphenyl

This invention relates to a process for the manufacture of 4,4'-dihydroxydiphenyl (biphenol, diphenol) and more particularly relates to a process for the purification of 4,4'-dihydroxydiphenyl which contains 4-monohydroxydiphenyl impurity.

Biphenol is useful as a reactant in condensation polymerisations and is particularly useful in forming phenolic type resins having good temperature resistance.

Biphenol was formed in the prior art by various methods. For example, halogenated diphenyl could be hydrolysed (U.S. Patent 3,413,341) or diphenyl could possibly be directly hydroxylated with peroxide in the presence of a suitable catalyst (U.S. Patent 3,453,332).

One of the most suitable methods for the preparation of biphenol is sulphonation of diphenyl to form diphenyldisulfonic acid which is then reacted with an alkali metal hydroxide or alkali metal salt to form a diphenylsulphonic acid salt followed by fusion of the diphenylsulphonic acid salt with an alkali metal hydroxide to form the sodium salt of biphenol followed by dissolving of the reaction mass and acidification to form biphenol. Such processes are described in U.S. Patent 2,368,361 and co-pending Patent Application 071,572 filed August 31, 1979.

In all of the prior art processes and especially in those involving fusion reaction, a significant quantity, i.e., in excess of 1%, of 4-monohydroxydiphenyl is formed. In fusion reactions, this is due to the presence of diphenylmonosulphonic acid salt which is formed during sulphonation of diphenyl and which is exceedingly difficult to remove from the desired diphenyl disulphonic acid salt. Such impurities in hydrolysis of halogenated diphenyl result from the presence of monohalogenated diphenyl products which occur during the halogenation process and which are also difficult to remove from the dihalodiphenyl compounds. Similarly, direct hydroxylation with peroxide can result in the attachment of a single OH group which will result in undesired monohydroxy impurity.

Such monohydroxydiphenyl impurity is especially significant when biphenol is formed from fusion type reactions. In the past, purification methods usually employed to purify the biphenol product have been ineffective to remove monohydroxydiphenyl. Recrystallisation is ineffective since the recrystallised product also contains recrystallised monohydroxydiphenyl. Distillation is ineffective due to the close boiling temperatures of monohydroxy and dihydroxydiphenyl and sublimation is ineffective since the monohydroxydiphenyl sublimes at a temperature close to the sublimation temperature of dihydroxydiphenyl and if anything, results in an increased concentration of monohydroxydiphenyl impurities since during sublimation, there is a higher concentration of monohydroxydiphenyl during the first part of the sublimation process. The presence of monohydroxydiphenyl in the 4,4'-dihydroxydiphenyl product is believed to be undesirable since when the 4,4'-dihydroxydiphenyl is used in a polymerisation, it is believed that the monohydroxydiphenyl acts as a chain terminator thus preventing the formation of polymers with molecular weights which are as high as would be obtainable in the absence of the monohydroxydiphenyl impurity.

It had been previously thought that the removal of the monohydroxydiphenyl impurity was much too costly since no inexpensive standard purification means appeared to efficiently accomplish the purification.

The present invention provides a process for purifying 4,4'-dihydroxydiphenyl which comprises contacting a solution of an alkali metal salt of 4,4'-dihydroxydiphenyl with activated carbon, removing the activated carbon from the solution and acidifying the solution with sufficient acid to convert essentially all of the 4,4'-dihydroxydiphenyl alkali metal salt to water insoluble 4,4'-dihydroxydiphenyl. The purification process results in removal of almost all of the 4-monohydroxydiphenyl impurity to obtain a product which generally contains less than 0.45 weight percent 4-monohydroxydiphenyl, usually less than 0.2 weight percent, and often less than 0.1 weight percent 4-monohydroxydiphenyl impurity.

The purification process is particularly applicable to a process for the preparation of 4,4'-dihydroxydiphenyl by fusion reaction of an alkali metal hydroxide with an alkali metal diphenyl disulphonate to form an alkali metal salt of 4,4'-dihydroxydiphenyl wherein the reaction is contacted with sufficient water to dissolve essentially all water soluble components of the mass to form a first solution; separating the resulting solution from insolubles; acidifying the solution into a sufficiently low pH to precipitate essentially all 4,4'-dihydroxydiphenyl product and separating the precipitated product from the remaining liquid. In accordance with the invention process, the first solution obtained by dissolving the reaction mass is contacted with activated carbon at 0 to 100°C for more than about 1 minute prior to separating the resulting solution from insolubles including the activated carbon.

Optionally, for even better purification, a second solution may be formed by dissolving the resulting precipitated product in sufficient aqueous liquid having a sufficiently high pH to cause the product to dissolve as an alkali metal salt of 4,4'-dihydroxydiphenyl; contacting the resulting second solution with activated carbon at 0 to 100°C for more than 1 minute; separating the solution from insolubles; acidifying the second solution to a sufficiently low pH to precipitate essentially all of the 4,4'-dihydroxydiphenyl product; and separating the product precipitated out of the second solution from remaining liquid.

Alternatively, but not preferably, the first solution need not be contacted with activated carbon and the 4,4'-dihydroxydiphenyl product can be precipitated followed by separating the precipitated product from the remaining liquid. The precipatated product may then be redissolved in aqueous liquid having a sufficiently

high pH to cause the product to dissolve and then activated carbon may be contacted with (e.g., be slurried into) the resulting second solution at 0 to 100°C for more than one minute. The insolubles may then be separated from the second solution, e.g., by filtration. The second solution may then be acidified to a sufficiently low pH to precipitate essentially all of 4,4'-dihydroxydiphenyl product and the product may be separated from the remaining liquid.

In each of the above cases, substantial quantities of monohydroxydiphenyl impurity are removed from the 4,4'-dihydroxydiphenyl desired product. It has unexpectedly been found that better removal is obtained when the activated carbon is slurried into the solution first formed by dissolving the initial reaction mass.

When 4,4'-dihydroxydiphenyl product is obtained from other processes, the product may, of course, be dissolved in sufficient aqueous liquid having a sufficiently high pH to cause the product to dissolve as an alkali metal salt of 4,4'-dihydroxydiphenyl followed by contacting the resulting solution with activated carbon at 0 to 100°C for more than 1 minute. The solution may then be acidified to a sufficiently low pH precipitate essentially all 4,4'-dihydroxydiphenyl product and a purified product may be separated from the remaining liquid.

In accordance with the invention, there is provided a process which permits purification of biphenol to remove essentially all 4-monohydroxydiphenyl impurity. In particular, the method comprises contacting a solution of 4,4'-dihydroxydiphenyl alkali metal salt with activated carbon followed by removing the activated carbon from the solution and acidifying the solution with sufficient acid to convert essentially all of the 4,4'-dihydroxydiphenyl alkali metal salt to water insoluble 4,4'-dihydroxydiphenyl. Unexpectedly, activated carbon selectively removes 4-mono-hydroxydiphenyl alkali metal salt from the solution.

The invention is applicable to remove 4-monohydroxydiphenyl impurity from 4,4'-dihydroxydiphenyl regardless of how the 4,4'-dihydroxydiphenyl is manufactured. The 4,4'-dihydroxydiphenyl can be manufactured by hydrolysis of halogenated diphenyl or by direct hydroxylation of diphenyl with peroxide or by sulphonation of diphenyl followed by reaction with an alkali metal hydroxide to form the alkali metal salt and the fusion of the metal salt with hydroxide to form the alkali metal salt of biphenol.

"Sufficient acid" means a ratio of acid to biphenol salt metal hydroxide of 1:1 in unit equivalent weights.

As used herein, "convert essentially all" means that 95% conversion is obtained. "Remove essentially all" means that 4-monohydroxydiphenyl impurity is reduced in the 4,4'-dihydroxydiphenyl, to a concentration of less than about 0.45 percent by weight of final product.

"Activated carbon" means any porous carbon in granular form which has not already absorbed its capacity of organic materials. In general, the activated carbon has an average particle size from 10 to 75 microns and an effective surface area of 1000 to 3000 square metres per gram.

Usually from about 7 to about 40 weight percent activated carbon by weight of dissolved 4,4'-dihydroxydiphenyl alkali metal salt is slurried into the solution; however, when activated carbon is used, having a large average particle size, i.e., in excess of 50 microns, larger percentages of the carbon may be used.

The 4,4'-dihydroxydiphenyl (biphenol) may be purified by dissolving the biphenol in an aqueous liquid having a sufficiently high pH to cause the product to dissolve. In general, the sufficiently high pH is above about 11.0. In general, the amount of water used to dissolve the product is from 2 to 20 millilitres of water per gram of reaction mass, i.e., combined biphenol salt, reactants, by-products and impurities and sufficient base to obtain a sufficiently high pH. Activated carbon is slurried into the resulting solution at 0 to 100°C. Higher temperatures are not needed or required but may be used when the solution is under pressure to permit the aqueous solution to reach a higher temperature before boiling. Contact time of the activated carbon with the solution is generally for an excess of 1 minute. Optimumly, the contact time is from 1 to 60 minutes. Longer contact times may be used; however, additional removal of monohydroxydiphenyl due to the increased contact time is found to be minimal.

After contacting the activated carbon with the solution, the activated carbon is removed by any suitable means such as filtration or centrifuging. The solution is then acidified to a sufficiently low pH to precipitate essentially all 4,4'-dihydroxydiphenyl product. The sufficiently low pH is generally 1 to 10 and is preferably from 1 to 5. The resulting purified product is then separated from the remaining liquid. The product is generally found to contain less than 0.45 weight percent monohydroxydiphenyl impurity. The impurity, in fact, is often less than 0.2 weight percent and is sometimes less than 0.1 weight percent depending upon solution pH's contact time, product conecentration and activated carbon specifications. Usually, the sufficiently low pH is obtained by adding any suitable inorganic acid such as hydrochloric acid, sulphuric acid, nitric acid or a phosphoric acid. The sufficiently high pH is usually obtained by adding alkali metal hydroxide such as potassium or sodium hydroxide.

When the 4,4'-dihydroxydiphenyl is prepared by fusion reaction of an alkali metal hydroxide with an alkali metal diphenyldisulphonate to form the alkali metal salt of 4,4'-dihydroxydiphenyl, followed by contacting the resulting reaction mass with sufficient water to dissolve essentially all water soluble components of the mass to form a first solution; separating the resulting solution from the insolubles; acidifying the solution to a sufficiently low pH to precipitate essentially all 4,4'-dihydroxydiphenyl product and separating the precipitated product from remaining liquid; the product may be purified by contacting the first solution with activated carbon at from about 9 to 100°C for more than about 1 minute prior to separating the solution from insolubles.

The resulting product then generally contains less than 0.45 weight percent of monohydroxydiphenyl

impurity. The product may then be further purified by forming a second solution by dissolving the resulting precipitated product in sufficient aqueous liquid, as previously discussed, having a sufficiently high pH to cause the product to dissolve as the 4,4'-dihydroxydiphenyl alkali metal salt. The resulting second solution is then contacted with activated carbon at a temperature of 0 to 100°C for more than 1 minute and the activated carbon is removed. The second solution is then treated with an acid to obtain a sufficiently low pH to precipitate essentially all 4,4'-dihydroxydiphenyl product and the precipitated product is then separated from remaining liquid.

In accordance with the purification process of the invention, the activated carbon may be contacted with the solution by any suitable means. Examples of such means include slurrying the carbon into the solution or passing the solution through a column containing the activated carbon. All that is required is that the solution be intimately contacted with the activated carbon.

When biphenol is prepared by a fusion reaction of an alkali metal diphenyldisulphonate with an alkali metal hydroxide, it has been unexpectedly found that better removal of monohydroxydiphenyl impurity is obtained when the dissolved reaction mass is contacted with activated carbon rather than first precipitating biphenol from the reaction mass and then redissolving the biphenol in a second solution which is contacted with the activated carbon. Desirably, the first solution formed by dissolving the reaction mass is contacted with activated carbon up to 15 and most preferably up to 60 minutes.

The following Examples serve to illustrate the present invention:

Example 1

3000 grams of potassium hydroxide flakes (90% KOH) are melted at from about 230 to about 250°C. 2000 grams of dipotassium diphenyldisulphonic acid are then slowly added to the melted potassium hydroxide and the mixture is heated to form about 335 to 340°C. After three hours, the temperature is increased to 360°C and the reaction mixture is poured into a stainless steel pan to cool. After the reaction mass is solidified, it is broken up. 200 grams of the reaction mass is dissolved in 500 millilitres of hot water. The solution is filtered through a flock bed and washed with 50 millilitres of additional hot water. 190 millilitres of 36% HCl is added to the solution to adjust the pH to 1.7 and the solution is agitated for 1 hour at from 90 to 95°C. The resulting insoluble product is separated by filtration at 90°C and washed with 1000 millilitres of hot distilled water. The product is then dried under a vacuum at 100°C. An analysis of the resulting product is set forth in Table 1 below.

Example 2

Example 1 is repeated except that 7.73 grams of activated carbon having a surface area of from 1400 to 1800 square metres per gram and an average particle size of smaller than 44 microns with about 15% of the particles having a particle size larger than 74 microns was added to the solution of the fusion mass in water. The activated carbon used is 20% by weight based on the theoretical amount of biphenol present. The mixture of the activated carbon and solution is held at 70°C for 30 minutes before it is filtered through a flock bed. The analysis of the resulting product is shown in Table I below.

Example 3

Example 1 is repeated except that the resulting product is not dried. It is slurried into 500 millilitres of hot water and 22 millilitres of 50% sodium hydroxide solution is added to dissolve the product. 7.73 grams of activated carbon, as previously described, is added to the solution and agitated at 70°C for 1/2 hour. The solution is then filtered through a flock bed. The analysis of the resulting product is shown in Table I below.

TABLE I

Example	%Strength	%Monohydroxy	Ash	Melting Point °C	Na	Ca	K
1	97.1	1.6	0.34	279.5	67	24	1283
2	100.3	0.16	0.33	279.2	54	47	838
3	102.2	0.42	0.09	282.2	70	29	81

A comparison of the foregoing Examples illustrates that the use of activated carbon is exceedingly effective in removing monohydroxydiphenyl impurity. A comparison of the Examples also shows that the most effective removal is obtained when the fusion reaction mass is dissolved and treated without previously precipitating the biphenol product (Example 2); but some removal is obtained whenever the activated carbon is used (Example 3).

Even better results are obtained when the product, as prepared in Example 2, is redissolved and retreated with activated carbon. In such cases, the monohydroxydiphenyl present is usually less than 0.1 weight percent. Low percentages, i.e. less than 0.1 weight percent, can also be obtained with large quantites of activated carbon, e.g. over 30% by weight biphenol, which may be obtained in the manner described in Example 2.

CLAIMS

1. A process for purifying 4,4'-dihydroxydiphenyl which comprises contacting a solution of an alkali metal salt of 4,4'-dihydroxydiphenyl with activated carbon, removing the activated carbon from the solution and acidifying the solution with sufficient acid to convert essentially all of the 4,4'-dihydroxydiphenyl alkali metal salt to water-insoluble 4,4'-dihydroxydiphenyl.

2. In a process for the preparation of 4,4'-dihydroxydiphenyl by:

a) fusion reaction of an alkali metal hydroxide with an alkali metal diphenyl disulphonate to form an alkali metal salt of 4,4'-dihydroxydiphenyl;

b) contacting the resulting reaction mass with sufficient water to dissolve essentially all water soluble components of the mass to form a first solution;

c) separating the resulting solution from insolubles;

d) acidfying the solution to a sufficiently low pH to precipitate essentially all of the 4,4'-dihydroxydiphenyl product; and

e) separating the precipitated product from remaining liquid;

the improvement which comprises:

f) contacting the first solution with activated carbon at 0 to 100°C for more than 1 minute prior to separating the resulting solution from insolubles.

3. A process according to claim 2 wherein the improvement further comprises:

g) forming a second solution by dissolving the resulting precipitated product in sufficient aqueous liquid having a sufficiently high pH to cause the product to dissolve as an alkali metal salt of 4,4'-dihydroxydiphenyl;

h) contacting the resulting second solution with activated carbon at 0 to 100°C for more than one minute;

i) removing the activated carbon from the solution;

j) acidifying the second solution to a sufficiently low pH to precipitate essentially all of the 4,4'-dihydroxydiphenyl product; and

k) separating the product precipitated out of the second solution from remaining liquid.

4. A process for the purification of 4,4'-dihydroxydiphenyl which comprises:

a) forming a solution by dissolving the 4,4'-dihydroxydiphenyl in an aqueous liquid having a sufficiently high pH to cause the product to dissolve;

b) slurrying activated carbon into the resulting solution at 0 to 100°C for more than 1 minute;

c) removing the activated carbon from the solution:

d) acidifying the solution to a sufficiently low pH to precipitate essentially all of the 4,4'-dihydroxydiphenyl product; and

e) separating the resulting product from remaining liquid.

5. A process according to claim 2 or 3 wherein the first solution is contacted with activated carbon for up to 60 minutes.

6. A process according to claim 5 wherein the first solution is contacted with activated carbon for up to 15 minutes.

7. A process according to claim 3, 5 or 6 wherein the reaction mass is contacted with water at 0 to 100°C.

8. A process according to claim 2, 3 or 5 to 7 wherein 2 to 20 millilitres of water is used, per gram of reaction mass, to dissolve the reaction mass.

9. A process according to claim 8 wherein 2 to 4 millilitres of water is used, per gram of reaction mass, to dissolve the reaction mass.

10. A process according to any one of claims 2, 3 and 5 to 9 wherein the reaction mass is contacted with water at 0 to 100°C at atmospheric pressure.

11. A process according to claim 4 wherein the 4,4'-dihydroxydiphenyl is contacted with water at 0 to 100°C at atmospheric pressure.

12. A process according to any one of claims 2, 3 and 5 to 10 wherein, in step c), the resulting solution is separated from insolubles by means of filtration.

13. A process according to claim 1, 4 or 11 wherein the activated carbon is removed from the solution by filtration.

14. A process according to any one of claims 2, 3, 5 to 10 and 12 wherein the sufficiently low pH in step d) is below 10.

15. A process according to any one of claims 3, 5 to 10, 12 and 14 wherein the sufficently low pH in step d) is from 1 to 10 and the sufficiently high pH in step g) is above 11.0.

16. A process according to claim 4, 11 or 13 wherein the sufficiently low pH in step d) is from 1 to 10 and the sufficiently high pH in step a) is above 11.0.

17. A process according to any one of claims 2, 3, 5 to 10, 12, 14 and 15 wherein, in step e), the precipitated product is separated by filtration.

18. A process according to any one of claims 2, 3, 5 to 10, 12, 14, 15 and 17 wherein the first solution in step f) is contacted with activated carbon by slurrying from 7 to 40 weight percent activated carbon, by weight of dissolved alkali metal salt of 4,4'-dihydroxydiphenyl, into the first solution.

19. A process according to any one of claims 3, 5 to 10, 12, 14, 15 and 17 wherein both the first solution in step f) and the second solution in step h) are contacted with activated carbon by slurrying from 7 to 40 weight

percent activated carbon, by weight of dissolved alkali metal salt of 4,4'-dihydroxydiphenyl, into the first and second solutions.

20. A process according to claim 1, 4, 11, 13 or 16 wherein the solution is contacted with activated carbon by slurring from 7 to 40 weight percent activated carbon, by weight of dissolved alkali metal salt of 4,4'-dihydroxydiphenyl alkali metal salt, into the solution.

21. A process according to any one of the preceding claims wherein the activated carbon has an average particle size of 10 to 75 microns and an effective surface area of 1000 to 3000 square metres per gram.

22. A process according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

23. 4,4'-Dihydroxydiphenyl when prepared/purified by a process as claimed in any one of the preceding claims.

24. A composition 4,4'-dihydroxydiphenyl and having a 4-monohydroxydiphenyl content of less than 0.45 weight percent.

25. A composition comprising 4,4'-dihydroxydiphenyl and having a 4-monohydroxydiphenyl content of less than 0.2 weight percent.

26. A composition comprising 4,4'-dihydroxydiphenyl and having a 4-monohydroxydiphenyl content of less than 0.1 weight percent.

27. A composition according to any one of claims 24 to 26 when obtained by a process as claimed in any one of claims 1 to 23.

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