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(54) **PREPARATION METHOD AND APPLICATION OF LOW-CHLORINE EPOXY RESIN**

(57) The present application belongs to the technical field of epoxy resins, and more particularly relates to a preparation method and application of a low-chlorine epoxy resin, which aim to solve the problem of high chlorine impurity content of an epoxy resin. The preparation method includes the following steps: performing an aldol condensation reaction of a bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde under a first preset reaction condition to obtain a reaction product; adding a perfluoroalkane solution to the reaction product for extraction, standing and then sepa-

rating to obtain an extract phase and a raffinate phase, the extract phase including a fluorine-containing chlorinated product, the raffinate phase including a low-chlorine bisphenol A epoxy resin; and separating the extract phase from the raffinate phase, so as to achieve the purpose of separating a chlorine-containing bisphenol A epoxy resin from a chlorine-free bisphenol A epoxy resin, thereby obtaining the low-chlorine bisphenol A epoxy resin, wherein the chlorine content of the low-chlorine bisphenol A epoxy resin is lower than that of the bisphenol A epoxy resin before reaction.

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Description**FIELD OF THE PRESENT DISCLOSURE**

5 [0001] The present application relates to the technical field of epoxy resins, and more particularly, to a preparation method and application of a low-chlorine epoxy resin.

BACKGROUND OF THE PRESENT DISCLOSURE

10 [0002] Epoxy resins are widely used in various fields of the national economy due to their excellent physical and mechanical properties, chemical stability, chemical resistance, heat resistance and adhesiveness.

[0003] Chlorine residues are inevitable during the synthesis of epoxy resins. In the electronic industries such as copper-clad plates, photoresist, and chip adhesives, the total chlorine content of the epoxy resin is required to be 800 ppm or less, but is required to be rather lower especially in the high-end electronics industry, aerospace and other fields. Therefore, chlorine impurities in epoxy resins need to be removed to meet the demands of the electronics industry.

15 [0004] The conventional methods for removing chlorine from epoxy resins mainly include a multi-stage distillation method and a method for removing chlorine by chemical agents. The multi-stage distillation method consumes more energy, resulting in high cost. The method for removing chlorine by chemical agents can only remove part of inorganic chlorine, but is difficult to remove organic chlorine.

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SUMMARY OF THE PRESENT DISCLOSURE

[0005] In order to solve the problem of high chlorine content in epoxy resins, the present application provides a preparation method and application of a low-chlorine epoxy resin.

25 [0006] An embodiment of the present application is implemented as follows:

[0007] an embodiment of the present application provides a preparation method of a low-chlorine epoxy resin, the method including:

30 performing an aldol condensation reaction of a bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde under a first preset reaction condition to obtain a reaction product;
adding a perfluoroalkane solution to the reaction product for extraction, standing and then separating to obtain an extract phase and a raffinate phase, the extract phase including a fluorine-containing chlorinated product generated by the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and polyfluoroalkyl aldehyde, the raffinate phase including a low-chlorine bisphenol A epoxy resin; and
35 separating the extract phase from the raffinate phase, so as to achieve the purpose of separating the fluorine-containing chlorinated product from a chlorine-free bisphenol A epoxy resin, thereby obtaining the low-chlorine bisphenol A epoxy resin, wherein the chlorine content of the low-chlorine bisphenol A epoxy resin is lower than that of the bisphenol A epoxy resin before reaction.

40 [0008] In some embodiments, the perfluoroalkane is perfluoropentane, perfluorohexane or perfluorooctane.

[0009] In some embodiments, the polyfluoroalkyl aldehyde is perfluorohexyl aldehyde, or perfluorooctyl aldehyde.

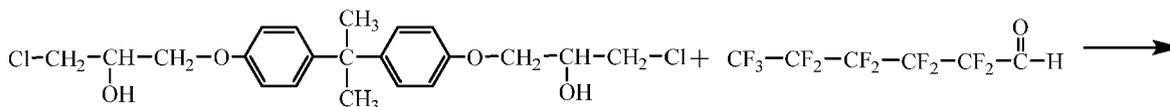
[0010] In some embodiments, a molar ratio of the bisphenol A epoxy resin to the polyfluoroalkyl aldehyde is 1: (2.1 to 2.3).

45 [0011] In some embodiments, the first preset reaction condition includes: a reaction temperature is 30°C to 45°C, a reaction time is 2 to 3 h, and a pH of the reaction solution during the reaction process is greater than 7.

[0012] In some embodiments, prior to the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde, the method further includes: mixing the bisphenol A epoxy resin containing chlorine impurities with the polyfluoroalkyl aldehyde homogeneously, and dissolving the mixture in cyclohexane.

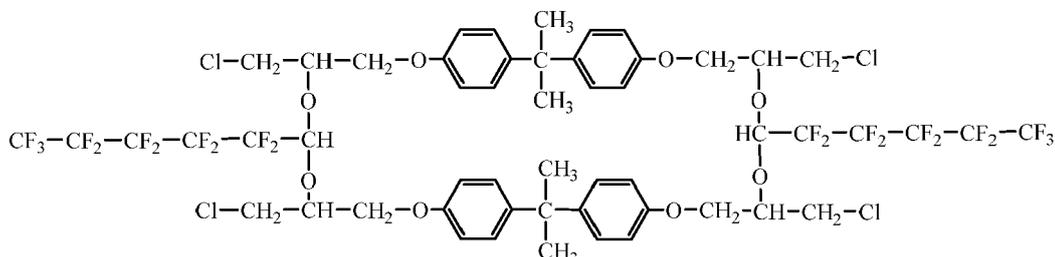
50 [0013] In some embodiments, a reaction principle of the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde to provide the fluorine-containing chlorinated product is as follows:

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[0014] Another embodiment of the present invention provides an application of a low-chlorine epoxy resin, including the application of the low-chlorine epoxy resin in a copper-clad plate.

[0015] The present application has the following beneficial effects: a hydroxyl group in the bisphenol A epoxy resin containing chlorine impurities undergoes an aldol condensation reaction with an aldehyde group in the perfluorohexyl aldehyde to generate the fluorine-containing chlorinated product; further, due to the great difference in solubility between the fluorine-containing chlorinated product and the low-chlorine epoxy resin, perfluoroalkane is thus selected as an extraction agent, only the fluorine-containing chlorinated product can be dissolved in the perfluoroalkane, and the extract phase is separated from the raffinate phase, so as to achieve the purpose of separating the fluorine-containing chlorinated product from the chlorine-free bisphenol A epoxy resin, thereby obtaining the low-chlorine bisphenol A epoxy resin.

[0016] The method of the present application has the characteristics of low cost, easy operation and high separation efficiency. The chlorine content of the prepared low-chlorine bisphenol A epoxy resin is less than 150 ppm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] To describe the examples of the present application or the technical solutions in the prior art more clearly, the accompanying drawings required for describing the examples or the descriptions in the prior art are briefly introduced as following. Apparently, the accompanying drawings in the following description show merely some examples of the present application, and other drawings can be derived from these accompanying drawings by a person of ordinary skill in the art without any creative efforts.

[0018] Fig. 1 is a diagram of a reaction principle of an aldol condensation reaction of a bisphenol A epoxy resin containing chlorine impurities and perfluorohexyl aldehyde as provided by an embodiment of the present application.

DESCRIPTION OF THE EMBODIMENTS

[0019] In order to make the objectives, embodiments and advantages of the present application more clearly, the exemplary embodiments of the present application will be described clearly and completely in conjunction with the accompanying drawings in the exemplary examples of the present application. Apparently, the described exemplary examples are merely some examples, rather than all examples, of the present application.

[0020] It should be noted that the brief description of terms in the present application is only to facilitate the understanding of the embodiments described below, and is not intended to limit the embodiments of the present application. Unless otherwise indicated, these terms shall be understood in their common and ordinary meanings.

[0021] The technical solution provided by the present application is described in detail in conjunction with the specific examples. The following examples are carried out by taking a bisphenol A epoxy resin as an example. Of course, the preparation method of the low-chlorine epoxy resin of the present application is also applicable to other epoxy resins.

[0022] In an extraction method, an impurity-removal and purification of product is performed by extraction by use of the difference in solubility, so the extraction method has the characteristics of low cost, simple operation, and high separation efficiency. However, because the solubility of an epoxy resin free of chlorine impurities and the solubility of an epoxy resin containing chlorine impurities are not much different, direct purification by extraction is unavailable, so there is no technology to remove chlorine impurities from an epoxy resin by the extraction method in the prior art.

[0023] The present application provides a method for removing chlorine impurities from an epoxy resin by using an extraction method.

[0024] According to the present application, the difference in solubility between a low-chlorine bisphenol A epoxy resin and a bisphenol A epoxy resin containing chlorine impurities is increased first to improve the recognition of the two epoxy

resins to an extraction solvent; and then impurity-removal and purification are performed by using the extraction method so as to achieve the purpose of separating the low-chlorine bisphenol A epoxy resin.

[0025] Fig. 1 is a diagram of a reaction principle of an aldol condensation reaction of a bisphenol A epoxy resin containing chlorine impurities and perfluorohexyl aldehyde as provided by an embodiment of the present application.

[0026] As shown in Fig. 1, a hydroxyl group in a bisphenol A epoxy resin (because an impurity chlorine in an epoxy resin containing chlorine impurities is often located at an end group, and a hydroxyl group on a carbon adjacent to an end group chlorine has good activity) and an aldehyde group in perfluorohexyl aldehyde undergo an aldol condensation reaction to obtain a reaction product, wherein the reaction product includes a fluorine-containing chlorinated product generated by the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and poly-fluoroalkyl aldehyde, and a bisphenol A epoxy resin free of chlorine impurities that does not react with perfluorohexyl aldehyde due to low hydroxyl activity.

[0027] Due to the greater difference in solubility of the fluorine-containing chlorinated product and the epoxy resin, so the purpose of separating these two may be achieved by the extraction method.

[0028] For the selection of an extraction agent, as perfluoroalkane is a non-polar molecule and has the characteristics of being both insoluble in oil and water, the perfluoroalkane is selected as the extraction agent, and only the fluorine-containing chlorinated product can be dissolved in the perfluoroalkane to form an extract phase, and a low-chlorine bisphenol A epoxy resin of a bisphenol A epoxy resin free of chlorine impurities is a raffinate phase.

[0029] The extract phase and the raffinate phase are separated, that is, the purpose of separating the fluorine-containing chlorinated product from the bisphenol A epoxy resin free of chlorine impurities is achieved, and the low-chlorine bisphenol A epoxy resin is obtained.

[0030] Upon testing, the total chlorine content of the low-chlorine bisphenol A epoxy resin extracted by the method of the present application is lower than that of the bisphenol A epoxy resin before the reaction.

[0031] The present invention is further described below in conjunction with specific examples.

Example 1

[0032] 15.0 g of perfluorohexyl aldehyde is slowly added to 45.5 g of bisphenol A epoxy resin, and mixed homogeneously to obtain a mixture, and the mixture is dissolved in 63.5 g of cyclohexane solvent and reacted for 20 min.

[0033] Under an alkaline condition (that is, a pH of the reaction solution is greater than 7) and a reaction temperature is 30°C, perfluorohexyl aldehyde and a bisphenol A epoxy resin containing chlorine impurities undergo an aldol condensation reaction for 2 h to obtain a reaction product.

[0034] Perfluorobutane is selected and added to the reaction product, and extraction is performed. Because fluorine is a non-polar molecule and has the characteristics of being both insoluble in oil and water, only the fluorine-containing chlorinated product can be dissolved in perfluoroalkane, and a low-chlorine bisphenol A epoxy resin is obtained after the fluorine-containing chlorinated product is removed therefrom.

Example 2

[0035] 23.1 g of perfluorohexyl aldehyde is slowly added to 73.6 g of bisphenol A epoxy resin, and mixed homogeneously to obtain a mixture, and the mixture is dissolved in 96.4 g of cyclohexane solvent and reacted for 20 min.

[0036] Under an alkaline condition (that is, a pH of the reaction solution is greater than 7) and a reaction temperature is 40°C, perfluorohexyl aldehyde and a bisphenol A epoxy resin containing chlorine impurities undergo an aldol condensation reaction for 3 h to obtain a first reaction product.

[0037] Perfluorohexane is selected and added to the first reaction product, and extraction is performed. Because fluorine is a non-polar molecule and has the characteristics of being both insoluble in oil and water, only the fluorine-containing chlorinated product can be dissolved in perfluoroalkane, and a low-chlorine bisphenol A epoxy resin is obtained after the fluorine-containing chlorinated product is removed therefrom.

Example 3

[0038] 18.9 g of perfluorohexyl aldehyde is slowly added to 63.2 g of bisphenol A epoxy resin, and mixed homogeneously to obtain a mixture, and the mixture is dissolved in 89.6 g of cyclohexane solvent and reacted for 20 min.

[0039] Under an alkaline condition (that is, a pH of the reaction solution is greater than 7) and a reaction temperature is 35°C, perfluorohexyl aldehyde and a bisphenol A epoxy resin containing chlorine impurities undergo an aldol condensation reaction for 2 h to obtain a first reaction product.

[0040] Perfluoropentane is selected and added to the first reaction product, and extraction is performed. Because fluorine is a non-polar molecule and has the characteristics of being both insoluble in oil and water, only the fluorine-containing chlorinated product can be dissolved in perfluoroalkane, and a low-chlorine bisphenol A epoxy resin is obtained

after the fluorine-containing chlorinated product is removed therefrom.

Example 4

5 **[0041]** 21.6 g of perfluorohexyl aldehyde is slowly added to 75.5 g of bisphenol A epoxy resin, and mixed homogeneously to obtain a mixture, and the mixture is dissolved in 97.3 g of cyclohexane solvent and reacted for 20 min.

[0042] Under an alkaline condition (that is, a pH of the reaction solution is greater than 7) and a reaction temperature is 45°C, perfluorohexyl aldehyde and a bisphenol A epoxy resin containing chlorine impurities undergo an aldol condensation reaction for 3 h to obtain a first reaction product.

10 **[0043]** Perfluorooctane is selected and added to the first reaction product, and extraction is performed. Because fluorine is a non-polar molecule and has the characteristics of being both insoluble in oil and water, only the fluorine-containing chlorinated product can be dissolved in perfluoroalkane, and a low-chlorine bisphenol A epoxy resin is obtained after the fluorine-containing chlorinated product is removed therefrom.

15 Example 5

[0044] 19.7 g of perfluorohexyl aldehyde is slowly added to 65.8 g of bisphenol A epoxy resin, and mixed homogeneously to obtain a mixture, and the mixture is dissolved in 85.4 g of cyclohexane solvent and reacted for 20 min.

20 **[0045]** Under an alkaline condition (that is, a pH of the reaction solution is greater than 7) and a reaction temperature is 30°C, perfluorohexyl aldehyde and a bisphenol A epoxy resin containing chlorine impurities undergo an aldol condensation reaction for 3 h to obtain a first reaction product.

[0046] Perfluorohexane is selected and added to the first reaction product, and extraction is performed. Because fluorine is a non-polar molecule and has the characteristics of being both insoluble in oil and water, only the fluorine-containing chlorinated product can be dissolved in perfluoroalkane, and a low-chlorine bisphenol A epoxy resin is obtained after a fluorine-containing chlorinated product is removed therefrom.

25 **[0047]** The chlorine contents of the epoxy resin in Examples 1 to 5 are determined, and the results are shown in Table 1.

[0048] It can be seen from Table 1 that the method of the present application method can effectively remove chlorine impurities from the bisphenol A epoxy resin, and when a molar ratio of the perfluorohexyl aldehyde to the bisphenol A epoxy resin is 1: 2.1, the reaction temperature is 40°C, and it is reacted for 3 h, the optimal removal effect of chlorine impurities is achieved.

Table 1 Test results of chlorine content of epoxy resin in Examples 1 to 5

Items	Example 1	Example 2	Example 3	Example 4	Example 5
Initial chlorine content/ppm	932	1003	987	1135	914
Final chlorine content/ppm	134	32	42	50	34
Removal rate/%	85.7	96.8	95.8	95.2	96.35

40 **[0049]** A hydroxyl group in the bisphenol A epoxy resin containing chlorine impurities undergoes the aldol condensation reaction with an aldehyde group in the perfluorohexyl aldehyde to generate the fluorine-containing chlorinated product; further, due to the large difference in solubility between the fluorine-containing chlorinated product and the low-chlorine epoxy resin, perfluoroalkane is selected as the extraction agent, only the fluorine-containing chlorinated product can be dissolved in the perfluoroalkane, and the extract phase is separated from the raffinate phase, so as to achieve the purpose of separating the fluorine-containing chlorinated product from the chlorine-free bisphenol A epoxy resin, thereby obtaining the low-chlorine bisphenol A epoxy resin.

45 **[0050]** The method of the present application has the characteristics of low cost, easy operation and high separation efficiency. The chlorine content of the prepared low-chlorine bisphenol A epoxy resin is less than 150 ppm.

50 **[0051]** The above disclosure is a further detailed description of the present invention, but cannot be determined that the specific embodiments of the present invention are limited thereto. For a person of ordinary skill in the art to which the present invention belongs, without departing from the idea of the present invention, a number of simple deductions or replacements may be made, which should be considered as falling within the scope defined by the claims of the present invention.

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Claims

1. A preparation method of a low-chlorine epoxy resin, comprising:

5 performing an aldol condensation reaction of a bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde under a first preset reaction condition to obtain a reaction product;
 adding a perfluoroalkane solution to the reaction product for extraction, standing and then separating to obtain
 10 an extract phase and a raffinate phase, wherein the extract phase comprises a fluorine-containing chlorinated product generated by the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde, and the raffinate phase comprises a low-chlorine bisphenol A epoxy resin; and
 separating the extract phase from the raffinate phase, so as to achieve the purpose of separating the fluorine-
 15 containing chlorinated product from the chlorine-free bisphenol A epoxy resin, thereby obtaining the low-chlorine bisphenol A epoxy resin, wherein the chlorine content of the low-chlorine bisphenol A epoxy resin is lower than that of the bisphenol A epoxy resin before reaction.

2. The preparation method of the low-chlorine epoxy resin according to claim 1, wherein the perfluoroalkane is perfluoropentane, perfluorohexane or perfluorooctane.

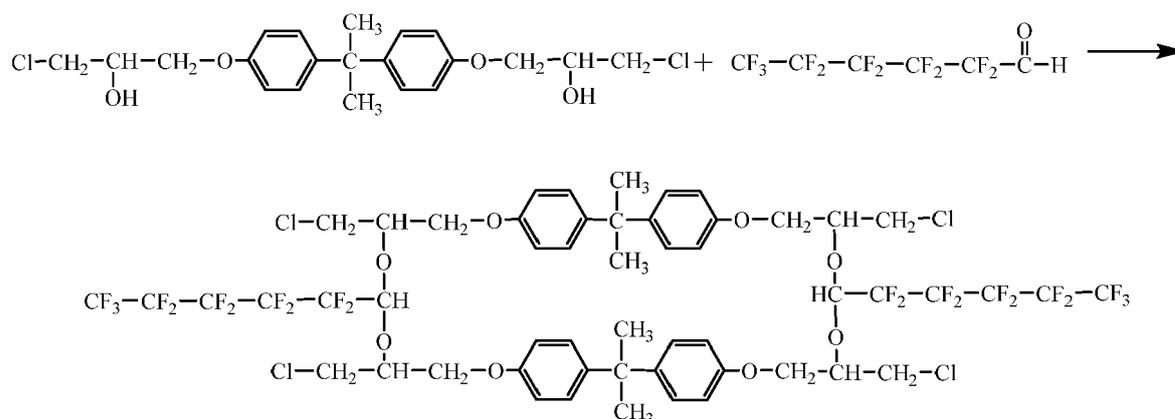
3. The preparation method of the low-chlorine epoxy resin according to claim 1, wherein the polyfluoroalkyl aldehyde is perfluorohexyl aldehyde, or perfluorooctyl aldehyde.

4. The preparation method of the low-chlorine epoxy resin according to claim 3, wherein a molar ratio of the bisphenol A epoxy resin to the polyfluoroalkyl aldehyde is 1: (2.1 to 2.3).

5. The preparation method of the low-chlorine epoxy resin according to claim 1, wherein the first preset reaction condition comprises: a reaction temperature of 30°C to 45°C, a reaction time of 2 to 3 h, and a pH of the reaction solution during the reaction process of greater than 7.

6. The preparation method of the low-chlorine epoxy resin according to claim 1, prior to the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and the polyfluoroalkyl aldehyde, the method further comprising:
 mixing the bisphenol A epoxy resin containing chlorine impurities with the polyfluoroalkyl aldehyde homogeneously,
 35 and dissolving the mixture in cyclohexane.

7. The preparation method of the low-chlorine epoxy resin according to claim 3, wherein a reaction principle of the aldol condensation reaction of the bisphenol A epoxy resin containing chlorine impurities and the polyfluorohexyl aldehyde for providing the fluorine-containing chlorinated product is as follows:



8. An application of a low-chlorine epoxy resin, comprising the application of the low-chlorine epoxy resin according to any one of claims 1 to 7 in a copper-clad plate.

