

SPECIFICATION

Quick-curing phenolic resin and process for preparing same

5 This invention relates to a quick-curing phenolic resin which is free from divalent metal salt and a process for producing said resin, and more particularly it provides a process for producing a high-ortho phenolic resin by reacting phenol and formaldehyde in a specified ratio under specified conditions without the need to use any divalent metal salt but by using a weak acid as catalyst, and to the high-ortho phenolic novolac resin obtained by said process.

10 Since H. L. Bender et al reported that a phenolic resin with a high ortho-linkage content can be produced by using a divalent metallic salt as catalyst and that such high-ortho phenolic resin has a quick-curing property, various process for producing such a high-ortho phenolic resin have been devised.

20 According to any of these conventional techniques, a divalent metal salt metal is always used in some form, and it has been considered that production of high-ortho phenolic resin by use of an acid catalyst alone is impossible or industrially inexpedient. It is well known that divalent metal salts have ortho-orientation, but the studies of the present inventors revealed that, in the reactions between phenols and formaldehyde, the ortho orientation appears at the time of an addition reaction, and that when the condensation reaction is performed at a temperature of 100°C or less, said reaction advances under the preponderance of para-position even in the presence of a divalent metal salt, and consequently, a phenolic resin with a low ortho content is produced. It has thus been clarified that one of the essential conditions for obtaining a high-ortho phenolic resin with a high ortho content is that the condensation reaction is carried out at a temperature of 105°C or more at which the para selectivity is reduced. This is attributable to the fact that the kinetic energy of each molecule increases as the temperature rises, and hence the energy barrier at the ortho-position due to steric hindrance of the hydroxyl group is relatively reduced to an ignorable extent, causing a corresponding increase of the probability of the reaction at the ortho-position.

When a strong acid catalyst such as hydrochloric acid is used a high-para novolac is obtained. This is because para-condensation takes place preferentially as the reaction proceeds with a strong acid having a pKa value of not more than 1. The present inventors have found that ortho selectivity in the condensation stage increases when a weak acid having a pKa value of more than 1 is used as acid catalyst. It has thus been found that when $pK_a \leq 1$, the condensation reaction rate elevates and said reaction advances at a low temperature, so that the ortho-position energy barrier due to steric hindrance of the hydroxyl group dominates the reaction, giving rise to selective condensation at the para-position, and that when $pK_a > 1$, it becomes possible to effect the reaction at a high temperature of 105°C or more owing to a low condensation reaction rate, resulting in an increased probability of ortho condensation.

As a result of further studies on the said reaction in the light of these facts, the present inventors have found that high-ortho phenolic resin can be produced industrially with no need of using a divalent metal salt as catalyst by carrying out the reaction with a weak acid at a temperature of 150°C or more, at which there is not much difference in reaction rate between the ortho-position and the para-position of the phenol nucleus and the para orientation is weakened to give rise to ortho selectively.

According to this invention there is provided a quick-curing phenol-formaldehyde resin in which the ortho linkage to para linkage ratio is within the range of from 0.85 to 2.5 and the number-average molecular weight of the resin exclusive of free phenol is within the range of from 500 to 1,200 and which is advantageously completely free of divalent metal salt.

According to this invention, such a quick-curing phenolic resin can be produced by a method comprising reacting phenol (P) and formaldehyde (F) in a F/P molar ratio of 0.6 to 1.0 at a temperature of 105°C or more under atmospheric pressure or under pressure with at least one acid having a pKa value of $1 < pK_a < 10$ as catalyst.

The present invention accordingly provides a process for the manufacture of a phenol-formaldehyde resin having an ortho to para linkage (hereinafter referred to as o/p) ratio of 0.85 to 2.5 and a number average molecular weight exclusive of free phenol of 500 to 1,200, wherein phenol (P) and formaldehyde (F) are reacted in an F/P molar ratio of 0.6 to 1.0, using as catalyst at least one acid having a pKa value of $1 < pK_a < 10$, for at least 3 hours under atmospheric pressure or under pressure at a temperature of 105°C or more, advantageously in the absence of divalent metal salt.

The phenol-formaldehyde resin produced according to the process of this invention is of the type in which the o/p ratio is within the range of from 0.85 to 2.5, and the number-average molecular weight of the resin exclusive of free phenol (hereinafter expressed as Mn) is 500 to 1,200. For use as molding material, it is desirable that the o/p ratio is 1.0 to 1.5 and Mn is 700 to 900. Advantageously, the free phenol content of the resin is 9% by weight or less.

The weak acids usable as catalyst in this invention are those having a pKa value of more than 1 but less than 10 such as, for example, formic acid, acetic acid, oxalic acid, malonic acid, succinic acid, tartaric acid, citric acid, benzoic acid, salicylic acid, phthalic acid, fumeric acid and the like, and at least one of these acids is used for said purpose. The higher the pKa value of the acid used, the higher the ortho linkage content of the obtained phenolic resin, but an acid having a pKa value of not less than 10 is not suitable because of poor reactivity of the reaction system. The amount of the weak acid used is preferably 8×10^{-4} to 0.1 mole per mole of the phenol charged. When the amount is less than 8×10^{-4} mole, the reaction rate is too low to use the process in industry. When the amount is more than 0.1 mole, the reaction rate is not increased and hence such an amount of weak acid is not economical.

The formaldehyde used in this invention is advan-

tageously used in the form of formalin or paraformaldehyde. As it is essential to carry out the reaction at a temperature of 105°C or more at which para selectivity is weakened, it is generally necessary to keep the system under pressure when using formalin. For instance, when 37% formalin is used and the F/P ratio is 0.80, application of pressure of about 2 atm. is normally required.

The phenol-formaldehyde resin obtained according to the process of this invention has a higher range of o/p ratio than that (0.7 - 0.8) of ordinary high-para novolac and had excellent quick-curing characteristics. Therefore, when this resin is used as molding material, it shows quick curability, and also, as it need contain no divalent metal salt, it can be used for the applications where the absence of impurities is required. Because of the absence of any divalent metal salt, the resin has good electrical properties, and further, if a type of acid that is decomposed at a high temperature, such as formic acid or malonic acid, is used, the ionic content in the resin is drastically reduced to provide a molding material with very good electrical properties.

Further, since the amount of the residual acid

$$\text{o/p ratio} = \frac{\text{ortho-ortho linkage methylene protons} + \text{para-para linkage methylene protons}}{\text{1/2 ortho-para linkage methylene protons} + \text{1/2 ortho-para linkage methylene protons}}$$

Number-average molecular weight:

The number-average molecular weight was first determined by a vapour pressure equilibrium method and then this was corrected by the value for free phenol obtained by gas chromatography to determine the number-average molecular weight of the resin exclusive of free phenol.

Curability:

Measuring apparatus used:

JSR Curelastometer* (shown in U.S. Patent No. 3,479,858 and British Patent No. 1,126,995)

* Trade Mark

Measuring conditions:

Molding pressure: 100 kg/cm²
Angle of oscillation: 0.5°
Die temperature: 150°C

(Gel time was measured at 120°C)

Example 1

With 300 g of phenol was reacted 92.5 g of 88% paraformaldehyde (F/P = 0.85) under refluxing for 4 hours in the presence of 0.4 g of oxalic acid (the internal temperature varying from 120°C to 105°C), and the reaction product was dehydrated under normal pressure for 3 hours and taken out when the internal temperature had reached 160°C. There was obtained 306 g of a phenol-formaldehyde resin containing 6.8% of free phenol and having an o/p ratio of 0.9 and Mn of 900. To 100 parts of this resin was added 15 parts of hexamethylenetetramine, and the gel time (hereinafter referred to as GT) of the mixture was measured on a hot plate at 150°C. It was 65 seconds.

Comparative Example 1

With 300 g of phenol was reacted 220 g of 37% formalin (F/P = 0.85) under refluxing for 4 hours in the presence of 0.4 g of oxalic acid (internal tempera-

ture: 98°C), and the reaction product was dehydrated in the same way as in Example 1 to obtain 302 g of a phenolic resin containing 7.2% of free phenol and having an o/p ratio of 0.75 and Mn of 900. This resin was an ordinary high-para novolac phenolic resin and its GT on a hot plate was 86 seconds, which is longer than that of the resin of Example 1.

Moreover, by utilizing as epoxy curing agent a phenol-formaldehyde resin of this invention, which contains impurities only in a small amount, which is excellent in electrical properties and which may have various o/p ratios, there is provided a high-quality encapsulating molding material with delicate moldability, heat resistance, moisture resistance and electrical properties, etc.

The invention is now described in further detail referring to Examples and Comparative Examples, but the invention is not limited to these Examples. In the following Examples and Comparative Examples, all the "parts" and "%" are by weight unless otherwise specified. The o/p ratio, number-average molecular weight and curability were determined in the following way. O/p ratio: The amount of methylene protons was measured by a nuclear magnetic (NMR) method, and the o/p ratio was calculated from the following equation:

ture: 98°C), and the reaction product was dehydrated in the same way as in Example 1 to obtain 302 g of a phenolic resin containing 7.2% of free phenol and having an o/p ratio of 0.75 and Mn of 900. This resin was an ordinary high-para novolac phenolic resin and its GT on a hot plate was 86 seconds, which is longer than that of the resin of Example 1.

Comparative Example 2

With 300 g of phenol was reacted 92.5 g of 88% paraformaldehyde (F/P = 0.985) under the same conditions as in Example 1 in the presence of 0.4 g of 30% hydrochloric acid, and the reaction product was dehydrated in the same way as in Example 1 to obtain 307 g of a phenolic resin. This resin was a high-para novolac phenolic resin containing 6.5% of free phenol and having an o/p ratio of 0.7 and Mn of 900. The internal temperature during refluxing varied from 120°C to 100°C.

Example 2

With 300 g of phenol was reacted 217 g of 37% formalin (F/P = 0.84) for 5 hours in the sealed state in the presence of 7.5 g of formic acid, which is a high-temperature decomposed type catalyst, while maintaining the internal temperature at 125°C. The reaction product was brought back to normal pressure and the dehydrated in the same way as in Example 1 to obtain 304 g of a phenolic resin containing 5.2% of free phenol and having an o/p ratio of 1.3, Mn of 850 and GT of 59 seconds. This resin was mixed with hexamethylenetetramine, wood flour, stearic acid, etc., and kneaded by 120°C hot rolls for 3 minutes to obtain a molding material. The molded product obtained from this material had an insulation resistance of $2.0 \times 10^9 \Omega$ in the normal state and $8.4 \times 10^9 \Omega$ after a boiling treatment.

Comparative Example 3

A conventional quick-curing phenolic resin (free phenol content = 5.5%, o/p ratio = 1.3, $\bar{M}_n$ = 850) produced by using hydrochloric acid and zinc acetate (a divalent metal salt) as catalyst was prepared into a molding material and molded under the same conditions as in Example 2. The molded product had an insulation resistance of $1.2 \times 10^9 \Omega$ in the normal state and $2.3 \times 10^9 \Omega$ after a boiling treatment. The electrical properties of this product were far inferior to those of the product of Example 2.

Example 3

With 300 g of phenol was reacted 92.5 g of 88% paraformaldehyde (F/P = 0.85) under refluxing in the presence of 4 g of malonic acid (a high-temperature decomposed type catalyst) for 3 hours (internal temperature: 120°C), and the reaction product was treated in the same way as in Example 1 to obtain 300 g of a phenolic resin containing 5.8% of free phenol and having an o/p ratio of 1.8 and $\bar{M}_n$ of 850. This resin was mixed with hexamethylenetetramine and its curability was measured by using a Curelasmeter. The gel time was 3 min. and 39 sec., the maximum degree of cure was 9.2 kg and the curing rate was 8.0 kg/min. This resin was further treated to obtain a molding material in the same manner as in Example 2 and its moldability was examined by using a small-sized injection machine. This molding material showed the possible residence time in cylinder of 180 seconds and was capable of continuous molding.

Comparative Example 4

A conventional type quick-curing phenol-formandeyhde resin (free phenol content = 6.2%, o/p ratio = 1.8, $\bar{M}_n$ = 850) was prepared by using salicylic acid and zinc acetate which is a divalent metal salt, and the curability of this resin was measured by using a Curelasmeter under the same conditions as in Example 3. As a result, the gel time was 2 min. and 48 sec., the maximum degree of cure was 8.9 kg and the curing rate was 8.2 kg/min. The curing rate is equal to that of the product of Example 3 but the gel time is shorter. An examination of the moldability conducted in the same way as in Example 3 showed that the possible residence time in cylinder was 60 seconds, far shorter than the product of Example 3, and the molding material was incapable of continuous molding. The difference from Example 3 is that a divalent metal salt is contained in the resin and this impairs thermal stability in the cylinder.

Example 4

With 300 g of phenol was reacted 97.9 g of 88% paraformaldehyde (F/P = 0.9) in the sealed state in the presence of 5 g of succinic acid for 5 hours (internal temperature: 130°C), and the reaction product was brought back to normal pressure and resinified by raising the internal temperature stepwise to 160°C over 4 hours, whereby 302 g of resin containing 7.3% of free phenol and having an o/p ratio of 2.3, $\bar{M}_n$ of 900 and GT of 30 sec. was obtained.

Example 5

The resin of Example 2 with few catalyst residue was mixed with an epoxy resin, a flame retardant, a curing assistant, a coupling agent, a filler, and a

releasing agent, and the mixture was kneaded by hot rolls at 100°C for 10 minutes to obtain an epoxy encapsulating material. The molded product obtained from this material had a volume resistivity of $6.2 \times 10^8 \Omega$ in the normal state and $8.7 \times 10^8 \Omega$ after a boiling treatment. The GT on a hot plate was 80 seconds.

Comparative Example 5

The conventional type high-ortho novolac phenolic resin of Comparative Example 3 was formulated into a molding material and a molded product therefrom was evaluated in the same manner as in Example 5. It showed a volume resistivity of $9.1 \times 10^4 \Omega$ in the normal state and $2.4 \times 10^2 \Omega$ after a boiling treatment, both of which were far inferior to those of the product of Example 5.

The high-para novolac phenolic resin of Comparative Example 2 was washed with water to remove the remaining free phenol and catalyst and then subjected to the same treatment and evaluation as mentioned above. The volume resistivity of the molded product from this resin was $8.8 \times 10^4 \Omega$ in the normal state and $2.1 \times 10^2 \Omega$ after a boiling treatment, and the GT on a hot plate was 60 seconds. The electrical properties were still inferior to those of the product of Example 5 although the resin was subjected to a washing treatment. Thus, the use of the novolac phenolic resin of this invention as curing agent makes it possible to obtain an epoxy encapsulating material having far better electrical properties than the conventional novolac phenolic resins with no need for performing any specific washing treatment.

Comparative Example 6

With 300 g of phenol was reacted 114 g of 88% paraformaldehyde (F/P = 1.05) in the same way as in Example 4 in the presence of 5 g of succinic acid. As the reaction became violent when the internal temperature reached 145°C, the reaction product was rapidly taken out on a vat. This resin showed the following properties: free phenol content = 9.0%; o/p ratio = 2.7; $\bar{M}_n$ = 1,250; but it had almost no fluidity. Production on an industrial scale is impossible because of danger involved in said production. Generally, production of phenolic resins with an o/p ratio $\times 2.5$ and/or $\bar{M}_n > 1,200$ is accomplished by the risk of gelation and hardly carried out industrially.

Comparative Example 7

When 300 g of phenol and 60 g of 88% paraformaldehyde (F/P = 0.55) were reacted in the same way as in Example 1 in the presence of 0.4 g of oxalic acid, there was obtained 254 g of phenolic resin containing 10.5% of free phenol and having an o/p ratio of 0.85 and $\bar{M}_n$ of 450. This resin is not only poor in yield but is also difficult to handle because of its semi-solid state and hence not suited for industrial applications. It will be understood that, while the process of the invention renders the presence of a divalent metal salt unnecessary, a process in which a divalent metal salt is present as well as the essential weak acid catalyst is within the scope of the invention, although neither this process nor its product is presently preferred.

CLAIMS

1. A phenol - formaldehyde resin free from



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A conventional quick-curing phenolic resin (free phenol content = 5.5%, o/p ratio = 1.3, $\bar{M}_n$ = 850) produced by using hydrochloric acid and zinc acetate (a divalent metal salt) as catalyst was prepared into a molding material and molded under the same conditions as in Example 2. The molded product had an insulation resistance of $1.2 \times 10^6 \Omega$ in the normal state and $2.3 \times 10^6 \Omega$ after a boiling treatment. The electrical properties of this product were far inferior to those of the product of Example 2.

Example 3

With 300 g of phenol was reacted 92.5 g of 88% paraformaldehyde (F/P = 0.85) under refluxing in the presence of 4 g of malonic acid (a high-temperature decomposed type catalyst) for 3 hours (internal temperature: 120°C), and the reaction product was treated in the same way as in Example 1 to obtain 300 g of a phenolic resin containing 5.8% of free phenol and having an o/p ratio of 1.8 and $\bar{M}_n$ of 850. This resin was mixed with hexamethylenetetramine and its curability was measured by using a Curelasmeter. The gel time was 3 min. and 39 sec., the maximum degree of cure was 9.2 kg and the curing rate was 8.0 kg/min. This resin was further treated to obtain a molding material in the same manner as in Example 2 and its moldability was examined by using a small-sized injection machine. This molding material showed the possible residence time in cylinder of 180 seconds and was capable of continuous molding.

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A conventional type quick-curing phenol-formandeyhde resin (free phenol content = 6.2%, o/p ratio = 1.8, $\bar{M}_n$ = 850) was prepared by using salicylic acid and zinc acetate which is a divalent metal salt, and the curability of this resin was measured by using a Curelasmeter under the same conditions as in Example 3. As a result, the gel time was 2 min. and 48 sec., the maximum degree of cure was 8.9 kg and the curing rate was 8.2 kg/min. The curing rate is equal to that of the product of Example 3 but the gel time is shorter. An examination of the moldability conducted in the same way as in Example 3 showed that the possible residence time in cylinder was 60 seconds, far shorter than the product of Example 3, and the molding material was incapable of continuous molding. The difference from Example 3 is that a divalent metal salt is contained in the resin and this impairs thermal stability in the cylinder.

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With 300 g of phenol was reacted 97.9 g of 88% paraformaldehyde (F/P = 0.9) in the sealed state in the presence of 5 g of succinic acid for 5 hours (internal temperature: 130°C), and the reaction product was brought back to normal pressure and resinified by raising the internal temperature stepwise to 160°C over 4 hours, whereby 302 g of resin containing 7.3% of free phenol and having an o/p ratio of 2.3, $\bar{M}_n$ of 900 and GT of 30 sec. was obtained.

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The resin of Example 2 with few catalyst residue was mixed with an epoxy resin, a flame retardant, a curing assistant, a coupling agent, a filler, and a

releasing agent, and the mixture was kneaded by hot rolls at 100°C for 10 minutes to obtain an epoxy encapsulating material. The molded product obtained from this material had a volume resistivity of $6.2 \times 10^6 \Omega$ in the normal state and $8.7 \times 10^5 \Omega$ after a boiling treatment. The GT on a hot plate was 80 seconds.

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The conventional type high-ortho novolac phenolic resin of Comparative Example 3 was formulated into a molding material and a molded product therefrom was evaluated in the same manner as in Example 5. It showed a volume resistivity of $9.1 \times 10^4 \Omega$ in the normal state and $2.4 \times 10^{12} \Omega$ after a boiling treatment, both of which were far inferior to those of the product of Example 5.

The high-para novolac phenolic resin of Comparative Example 2 was washed with water to remove the remaining free phenol and catalyst and then subjected to the same treatment and evaluation as mentioned above. The volume resistivity of the molded product from this resin was $8.8 \times 10^4 \Omega$ in the normal state and $2.1 \times 10^{12} \Omega$ after a boiling treatment, and the GT on a hot plate was 60 seconds. The electrical properties were still inferior to those of the product of Example 5 although the resin was subjected to a washing treatment. Thus, the use of the novolac phenolic resin of this invention as curing agent makes it possible to obtain an epoxy encapsulating material having far better electrical properties than the conventional novolac phenolic resins with no need for performing any specific washing treatment.

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CLAIMS

1. A phenol - formaldehehyde resin free from

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divalent metal salt, which has an ortho linkage to para linkage ratio ranging from 0.85 to 2.5 and a number-average molecular weight of the resin exclusive of free phenol of 500 to 1,200.

5 2. A resin according to claim 1, wherein the free phenol content is 9% by weight or less.

3. A process for producing a phenol - formaldehyde resin free from divalent metal salt and having an ortho linkage to para linkage ratio of 0.85 - 2.5

10 and a number-average molecular weight of the resin exclusive of free phenol of 500 - 1,200 characterized in that phenol (P) and formaldehyde (F) are reacted for at least three hours in the F/P molar ratio of 0.6 - 1.0 with at least one acid having pKa value of $1 < pK_a < 10$ as catalyst, under atmospheric pressure or

15 under pressure at a temperature of 105°C or more.

4. A process according to claim 3 wherein the formaldehyde is in the form of formalin or paraformaldehyde.

20 5. A process according to claim 4, wherein the formaldehyde is used in the form of formalin and the reaction is carried out under pressure.

6. A process according to claim 3, wherein the formaldehyde is used in the form of paraformaldehyde and the reaction is carried out under atmospheric pressure.

7. A process as claimed in claim 3, carried out substantially as described in any one of Examples 1 to 4 herein.

30 8. A resin as claimed in claim 1, substantially as described in any one of Examples 1 to 5 herein.

9. A phenolic resin whenever prepared by a process as claimed in any one of the claims 3 to 7.

10. A process for producing a phenol-formaldehyde resin having an ortho linkage to para linkage ratio of 0.85 - 2.5 and a number-average molecular weight of the resin exclusive of free phenol of 500 - 1,200 characterized in that phenol (P) and formaldehyde (F) are reacted in the F/P molar ratio of 0.6 - 1.0 using at least one acid having a pKa value of $1 < pK_a < 10$ as catalyst, under atmospheric or under pressure at a temperature of 105°C or more, for at least 3 hours.

11. A phenolic resin whenever prepared by the process of claim 10.