

Quick-Curing Phenolic Resin, a Process
for its manufacture, and shaped
structures derived therefrom

1 This invention relates to an industrial
process for producing quick-curing phenolic resins.
The characteristic feature of this invention consists
in producing a high-ortho phenolic resin safely, easily
5 and at low cost by use of an appropriate combination of
a divalent metal salt effective for the addition reac-
tion and a divalent metal salt or an acid effective for
the condensation reaction.

 Since H.L. Bender et al. reported that a high-
10 ortho phenolic novolac resin having a high ortho linkage
content has a quick-curing property, a variety of
production processes have been proposed for this high-
ortho phenolic novolac resin.

 High-ortho phenolic novolac resins are usually
15 produced by first producing a methylol-phenol form with
a weakly acidic divalent metal salt as a catalyst,
followed by condensing the same. In this case, if the
reaction is carried out with only one kind of weakly
acidic divalent metal salt catalyst, it is difficult
20 to keep a good balance between the reaction velocities
of addition reaction (methylolation) and condensation
reaction (methylene formation) during the progress of
the reactions, so that there arise problems such that
the reaction system forms a gel, that ~~only~~ a phenolic
25 resin having ^{only} a small ortho/para linkage ratio is

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produced, and the like.

The present inventors have studied the reaction in detail and have discovered the role played by the divalent metal salt and the reaction mechanism in the production of a high-ortho phenolic resin, and as a result of their discoveries have invented an industrial production process which results in a high-ortho phenolic resin. The inventors have appreciated from their studies that the formation of a phenolic resin having a high ortho/para linkage ratio (hereinafter referred to as o/p ratio) using a divalent metal salt is only made possible by forming the ortho-methylol product by a reflux reaction and then condensing the ortho-methylol product at a temperature of more than 100°C, at which the para-selectivity of the reaction is weakened, whereas, if the condensation is carried out at a temperature of not more than 100°C, the condensation proceeds preferentially at the para-position even in the presence of a divalent metal salt, so that only a phenolic resin having a small o/p ratio is obtained. Further, it has also been found that the dissociation constant and solubility of the divalent metal salt determines the selectivity of the addition-condensation reaction, namely that a divalent metal salt having a low dissociation constant and a low solubility is effective for the addition reaction (methylation), while a divalent metal salt having a high dissociation constant and a high solubility is effective for the condensation reaction (methylene formation).

The present inventors have found that when

1 catalysts different in action are used in an appropriate
combination and the condensation reaction is carried out
at a temperature of more than 100°C, both addition
reaction and condensation reaction proceed with a good
5 balance, whereby a high-ortho type of quick-curing
phenolic resin can be produced safely, easily and
inexpensively.

According to this invention, there is provided
a process for producing a phenolic resin having an o/p ratio
10 of 0.9-3.0 and a number average molecular weight of the
resin exclusive of free phenol of 600-1,100, which comprises
reacting a phenol (P) and formaldehyde (F) in a F/P molar
ratio of 0.6-0.95:1 at a temperature of more than 100°C with
a combination of (A) a divalent metal salt catalyst effective
15 for the addition reaction and (B) a divalent metal salt
catalyst effective for the condensation reaction, said
combination being used from the start of the reaction, or
comprises subjecting said phenol and formaldehyde in a F/P
molar ratio of 0.6-0.95:1 to a reaction under reflux in the
20 presence of the (A) catalyst only to form an orthomethylol-
phenol product, adding an acid to the system until the pH
becomes 1-5 which is a value effective for the condensation
reaction, immediately thereafter removing water under
reduced pressure, and then subjecting the product to a
25 further reaction at normal pressure at a temperature of
more than 100°C. It is particularly effective to use one
or more salts of alkaline earth metals or transition

1 metals with organic monocarboxylic acids as the (A)
catalyst and one or more salts of alkaline earth metals
or transition metals with inorganic acids as the (B)
catalyst. The term "transition metals" used herein means
5 metals selected from the first and second series of
transition elements having atomic numbers of 21-30 and
39-48 in the Periodic Table. As said acid, it is effective
to select one or more acids having an optimum solubility
and dissociation constant for obtaining the desired pH
10 value. When a pH value of, for example, about 4 is desired,
it is preferable to use not a small quantity of hydro-
chlorid acid but a large amount of salicylic acid.

The molar ratio of the catalyst (A) to the
catalyst (B), when used in combination, is advantageously
15 0.02-4. When it is less than 0.02, the yield is extremely
low. When it is more than 4, there is a danger of gelation.
The amount of the divalent metal salt used is advantageous-
ly 0.1-3% by weight based on the weight of phenol charged.
That is, when the catalysts (A) and (B) are used in combi-
20 nation the total amount of both catalysts is advantageously
0.1-3% by weight based on the weight of phenol charged,
while when the catalyst (A) and an acid are used in combi-
nation the amount of the catalyst (A) is 0.1-3% by weight
based on the weight of phenol charged. When the amount of
25 the divalent metal salt is less than 0.1% by weight, the
yield is extremely low. When it is more than 3% by weight,
the salt content in the phenolic resin becomes

- 1 not negligible and may adversely affect the electrical properties.

When the catalyst (A) and an acid are used in combination, it is desired that the consumption of
5 formaldehyde is 50-95% by weight and the consumption of the phenol is 30-75% by weight, at the time of completing the reflux. If the consumptions are too small, a low molecular weight resol is mainly formed, so that the subsequent reaction is difficult to control and there
10 is a fear of gelation. If the consumptions are too great, the condensation reaction progresses excessively, and the phenolic resin obtained has a relatively low o/p ratio.

When the catalyst (A) and an acid are used in
15 combination, it is desired that the dehydration under reduced pressure after addition of the acid is effected until the water content of the reaction system becomes 5% by weight or less. In the step of dehydration under reduced pressure after addition of acid, it is desirable
20 to make the water content of the system not more than 5% by weight in order to suppress the generation of heat due to addition of acid, to make the reaction system approach a non-aqueous state, to accelerate the subsequent condensation reaction and to facilitate the
25 temperature control in the condensation reaction. When it is more than 5% by weight, the condensation temperature is kept in a low level owing to the heat of vaporization of water, so that only a phenolic resin

- 1 having a low o/p ratio is obtained.

As the formaldehyde source, it is preferable to use paraformaldehyde having a low water content when the catalysts (A) and (B) are used in combination and
5 to use formalin having a high water content when the catalyst (A) and the acid are used in combination. When the catalysts (A) and (B) are used in combination, the low water content, namely, the use of paraformaldehyde, is preferable for securing a temperature of more than
10 100°C at normal pressure. On the other hand, super-atmospheric pressure is required to secure a temperature of more than 100°C when formalin is used. When the catalyst (A) and the acid are used in combination, the use of formalin having a high water content is preferable
15 for controlling the addition reaction, absorbing the heat generated at the time of adding the acid and dispersing the reaction system uniformly. When paraformaldehyde is used in said case, the reaction is difficult to control.

20 The phenolic resin obtained according to this invention has an o/p ratio of 0.9-3.0 and a number average molecular weight of the resin exclusive of free phenol of 600-1,100. The desired o/p ratio can be obtained by varying the ratio of the catalyst (A) to
25 the catalyst (B) or by adjusting the pH value after addition of acid, and the desired molecular weight can be obtained by varying the F/P at the time of charge. That is, by this invention, resins having an o/p ratio

1 and a molecular weight falling in the above-mentioned
ranges can freely be obtained safely, easily and
inexpensively.

From the phenolic resin obtained by this
5 invention, there can be obtained molding materials
having various curability and flowability. Particularly,
a molding material formed from a phenolic resin having
an o/p ratio of 1.0-1.5 and a number average molecular
weight of the resin exclusive of free phenol of 700-900
10 exhibits the features that it has a good heat-stability,
a good flowability and a quick-curing property and
enables the shortening the molding time in a large
scale molding, whereby high cycle molding is made
possible. Further, owing to its excellent flowability
15 and melting property, addition of plasticizer becomes
unnecessary, so that problems such as dulling of mold,
bad appearance of molded product and the like can be
eliminated.

This invention is explained below referring
20 to Examples and Comparative Examples. The Examples are
by way of illustration and not by way of limitation.

In the following Examples and Comparative
Examples, the curability, the o/p ratio, the number
average molecular weight and the Barcol hardness were
25 determined in the following manner.

1) Curability

(RTM)

Instrument used: Curelastometer/as disclosed
in U.S. Patent No. 3,479,858 and

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1 British Patent No. 1,126,995.

Measuring Conditions

Die temperature: 150°C

Molding pressure: 100 kg/cm²

5 Angle of oscillation: 0.5°

2) o/p ratio

The amount of the protons of ortho-methylol, para-methylol, ortho-ortho bonded methylene, ortho-para bonded methylene and para-para bonded methylene was
10 measured by means of a nuclear magnetic resonance spectrometry (NMR), from which the ortho linkage/para linkage ratio was calculated from the following equation:

$$\text{o/p ratio} = \frac{\left(\begin{array}{c} 1/2 \text{ ortho-} \\ \text{methylol} \\ \text{methylene} \\ \text{protons} \end{array} \right) + \left(\begin{array}{c} \text{ortho-ortho} \\ \text{linkage} \\ \text{methylene} \\ \text{protons} \end{array} \right) + \left(\begin{array}{c} 1/2 \text{ ortho-para} \\ \text{linkage} \\ \text{methylene} \\ \text{protons} \end{array} \right)}{\left(\begin{array}{c} 1/2 \text{ para-} \\ \text{methylol} \\ \text{methylene} \\ \text{protons} \end{array} \right) + \left(\begin{array}{c} \text{para-para} \\ \text{linkage} \\ \text{methylene} \\ \text{protons} \end{array} \right) + \left(\begin{array}{c} 1/2 \text{ ortho-para} \\ \text{linkage} \\ \text{methylene} \\ \text{protons} \end{array} \right)}$$

3) Number average molecular weight

15 It was measured by a vapor pressure equilibrium method. The number average molecular weight of the resin exclusive of free phenols was calculated from the measured value of number average molecular weight and the amount of free phenols determined by gas chromatography.
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4) Barcol hardness

Apparatus: Barcol Impresser 935

Curing conditions: 175°C, 20 seconds

Time of measurement: 10 seconds after taking
the sample out of the mold.

Example 1

282 g of phenol and 87 g of 88% by weight para-
5 formaldehyde (F/P = 0.85) were subjected to reaction under
reflux for 3 hours in the presence of 1.96 g of zinc chloride
and 0.11 g of barium acetate. (The temperature inside the
reaction vessel varied from 115°C to 105°C) Subsequently,
the reaction mixture was dehydrated by heating at normal
10 pressure and taken out into a vat when the internal
temperature had reached 150°C. 285 g of a resin having an
o/p ratio of 1.1, a number average molecular weight of the
resin exclusive of free phenol of 805 and a free phenol
content of 7.0% by weight was obtained. To 100 parts by
15 weight of this resin was added 15 parts by weight of
hexamethylenetetramine, and the gel time was measured on
a hot plate kept at 150°C (hereinafter, this gel time is
referred to as "hot plate gel time"), and found to be 43
seconds. Further, 18 parts by weight of hexamethyl-
20 enetetramine, 65 parts by weight of woodflour, 25 parts
by weight of calcium carbonate and 3 parts by weight of
stearic acid were added to 100 parts by weight of this
resin and the mixture was kneaded on hot rolls at 100°C
for 5 minutes to obtain a molding material. This
25 material was formed into a molded article, which had a
Barcol hardness of 52. When a high-para novolac

- 1 phenol resin produced with a usual acid catalyst
(Comparative Example 4) was used, the Barcol hardness
was as low as 25 for the same formulation.

Example 2

- 5 282 g of phenol and 160 g of 45% by weight formalin
(F/P = 0.80) were subjected to reaction under reflux for
3 hours in the presence of 3.0 g of manganese
acetate (the consumption of phenol was 40% by weight and
the consumption of formaldehyde was 81% by weight).
- 10 Then, 0.1 g of 30% by weight hydrochloric acid was
added (pH 1.1), after which the mixture was dehydrated
under reduced pressure for 30 minutes (water content 1%).
Thereafter, the temperature was stepwise raised from
105°C to 150°C in 3 hours to obtain 285 g of a resin
- 15 having a free phenol content of 6.0% by weight, an o/p
ratio of 1.1 and a number average molecular weight of
the resin exclusive of free phenol of 750. This resin
had a hot plate gel time of 51 seconds. In the case of the
usual high-para novolac phenol resin, the gel time is
- 20 about 91 seconds. Further, the curability, i.e.
maximum degree of cure and curing rate, of the same
sample as used in the measurement of gel time was
measured by means of Curelastometer (a trade name of
Japan Synthetic Rubber). The results were as shown in
- 25 Table 1. The resin obtained in the present Example is
superior to high-para novolac phenol resin (Comparative
Example 4) in both maximum degree of cure and curing

- 1 rate, demonstrating its quick-curing property.

Comparative Example 1

In the same manner as in Example 2, 282 g of phenol and 195 g of 37% by weight formalin ($F/P = 0.80$) were subjected to reaction in the presence of 2.8 g of zinc chloride without adding hydrochloric acid and then taken out onto a vat. Thus, 240 g of a resin having a free phenol content of 6.2% by weight, an o/p ratio of 0.9, a number average molecular weight of the resin exclusive of free phenol of 650 and a hot plate gel time of 63 seconds was obtained. As compared with the products of Example 1 and Example 2, this resin was lower in not only o/p ratio and molecular weight but also yield.

15 Example 3

A mixture of 282 g of phenol and 81.8 g of 88% by weight paraformaldehyde ($F/P = 0.80$) was slowly heated from room temperature to 100°C in 30 minutes and then from 100°C to 150°C in one hour in the presence of 1.6 g of zinc chloride and 0.66 g of zinc acetate. Thereafter, the mixture was kept at a reduced pressure of 80 mm Hg and then taken out onto a vat. Thus, 289 g of a resin having a free phenol content of 7.6% by weight, an o/p ratio of 1.5, a number average molecular weight of the resin exclusive of free phenol of 850 and a hot plate gel time of 37 seconds was obtained. As

1 measured with Curelastometer, the curability of the
resin was as shown in Table 1. Further, a molding
material was prepared therefrom in the same manner as
in Example 1, and the Barcol hardness of a molded
5 article of the molding material was measured to be
found 57.

Example 4

282 g of phenol and 187 g of 37% by weight formalin
(F/P = 0.77) were subjected to reaction under reflux for
10 3 hours in the presence of 3.3 g of zinc
acetate (consumption of phenol, 60% by weight; consumption
of formaldehyde, 90% by weight), after which 4.1 g of
salicylic acid was added thereto (pH 3.5). After
dehydration under reduced pressure (water content, 2%
15 by weight), the mixture was slowly heated from 100°C to
150°C in 3 hours, to obtain 288 g of a resin having a
free phenol content of 5.8% by weight, an o/p ratio of
1.8, a number average molecular weight of the resin
exclusive of free phenol of 800 and a hot plate gel
20 time of 28 seconds. As measured with Curelastometer,
the curability of the resin was as shown in Table 1.
A molding material was prepared therefrom in the same
manner as in Example 1 and formed into a molded article.
The insulation resistance of the molded article was
25 $3.1 \times 10^{10} \Omega$ in the normal state and $5.7 \times 10^9 \Omega$ after
being boiled.

1 Comparative Example 2

282 g of phenol and 190 g of 37% by weight formalin were subjected to reaction under reflux for 2 hours in the presence of 1.6 g of zinc acetate (consump-
5 tion of phenol, 50% by weight; o/p ratio, 2.5). The mixture was heated for an additional 2 hours (consumption of phenol, 80% by weight; o/p ratio, 1.6). Then, 1.5 g of oxalic acid was added (pH 2.1), and the resulting mixture was heated under reflux for 2 hours. Thereafter,
10 the mixture was dehydrated and concentrated under normal pressure and then heated to 150°C in 3.5 hours, to obtain 285 g of a resin having a free phenol content of 7.0% by weight, an o/p ratio of 0.9, a number average molecular weight of the resin exclusive of free phenol
15 of 820 and a hot plate gel time of 51 seconds. These results demonstrate that the o/p ratio drops when the reaction is effected at a temperature of not more than 100°C even in the presence of a divalent metal salt and that the o/p ratio drops when the temperature of conden-
20 sation is not more than 100°C.

As compared with the resin of Example 3 and Example 4, this resin was lower in o/p ratio and inferior in quick-curing property. Moreover, it necessitated a reaction time of more than 2 hours longer
25 than that in Example 1, Example 2, Example 3 and Example 4.

1 Example 5

In the same manner as in Example 1, 286 g of a resin was prepared by reacting 282 g of phenol and 79 g of 88% by weight paraformaldehyde ($F/P = 0.77$) in the presence of 0.8 g of manganese nitrate and 1.9 g of zinc acetate. This resin had a free phenol content of 6.0% by weight, an o/p ratio of 2.0, a number average molecular weight of the resin exclusive of free phenol of 900 and a hot plate gel time of 23 seconds. A molding material was prepared therefrom in the same manner as in Example 1, and formed into a molded article. It had a Barcol hardness of 60.

Example 6

282 g of phenol and 195 g of 37% by weight formalin ($F/P = 0.80$) were subjected to reaction under reflux for 3.5 hours in the presence of 1.5 g of manganese acetate (consumption of phenol, 50% by weight; consumption of formaldehyde, 93% by weight). After adding 1.0 g of benzoic acid (pH 5.0), the mixture was immediately concentrated under reduced pressure (water content, 3% by weight). Then, the mixture was stepwise heated to 150°C in 3 hours, to obtain 292 g of a resin having a free phenol content of 8.0% by weight, an o/p ratio of 2.5 and a number average molecular weight of the resin exclusive of free phenol of 900. As measured with Curelastometer, the curability of this resin was as shown in Table 1.

Comparative Example 3

282 g of phenol and 160 g of 45% by weight formalin were subjected to reaction under reflux for 3 hours in the presence of 3.0 g of manganese acetate and 0.1 g of 30% by weight hydrochloric acid. Then, the mixture was subjected to dehydration in the same manner as in Example 2, and taken out onto a vat. The resin thus obtained was a high-para phenol novolac resin. Although in the present Example the F/P, the catalysts, and the amount of catalysts were the same as in Example 2, no high-ortho resin was obtained because the hydrochloric acid was added at once at the start of reaction.

Comparative Example 4

282 g of phenol and 195 g of 37% by weight formalin were subjected to reaction under reflux for 3 hours in the presence of 3 g of oxalic acid, after which the mixture was dehydrated under normal pressure and heated to 150°C in 4 hours. The resin thus obtained was a high-para phenol novolac resin having a free phenol content of 7% by weight, an o/p ratio of 0.75 and a number average molecular weight of the resin exclusive of free phenol of 850. The curability of this resin was measured with Curelastometer in the same manner as in Example 2. The results were as shown in Table 1, which demonstrate that the curing reaction of this resin is much slower than that of the resins obtained

1 in the Examples.

Comparative Example 5

In the same manner as in Example 2, 282 g of phenol and 170 g of 37% by weight formalin (F/P = 0.70) were reacted in the presence of 3.3 g of zinc acetate without adding hydrochloric acid. When the inner temperature reached 145°C, a violent reaction took place and a gel was formed.

Table 1. Curability measured with Curelastometer

	Example 2	Example 3	Example 4	Example 6	Compara- tive Example 4
Maximum degree of cure (kg)	9.0	8.7	8.5	7.5	6.2
Curing rate (kg/ min)	3.8	5.2	5.8	8.1	2.1



CLAIMS

1. A process for producing a phenolic resin having an ortho linkage/para linkage ratio of 0.9-3.0 and a number average molecular weight of the resin exclusive of free phenol of 600-1,100, which comprises reacting a phenol and formaldehyde in the ratio of one mole of the phenol to 0.6-0.95 mole of formaldehyde at a temperature of more than 100°C with a combination of (A) a divalent metal salt catalyst effective for the addition reaction with (B) a divalent metal salt catalyst effective for the condensation reaction, said catalysts (A) and (B) being used from the start of the reaction, or comprises reacting a phenol and formaldehyde in the ratio of 1 mole of the phenol to 0.6-0.95 mole of formaldehyde under reflux in the presence of said catalyst (A), then adding an acid to adjust the pH value to 1-5, immediately thereafter removing water under reduced pressure and further reacting the product under normal pressure at a temperature of more than 100°C.
2. A process according to Claim 1, wherein catalyst (A) is one or more salts of an organic mono-carboxylic acid with an alkaline earth metal or a transition metal selected from the first and the second series of transition elements having atomic numbers of 21-30 and 39-48 in the Periodic Table.
3. A process according to Claim 1, wherein said catalyst (B) is one or more salts of an inorganic acid with an alkaline earth metal or a transition metal selected from the first and the second transition



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elements having atomic numbers of 21-30 and 39-48 in the Periodic Table.

4. A process according to Claim 3, wherein the combination of the catalyst (A) with the catalyst (B) is used, the molar ratio of the catalyst (A) to the catalyst (B) is 0.02-4, and the total amount of the catalysts is 0.1-3% by weight based on the weight of the phenol charged.

5. A process according to Claim 3 or 4, wherein the combination of the catalyst (A) with the catalyst (B) is used and the formaldehyde is used in the form of paraformaldehyde.

6. A process according to Claim 1 or 2, wherein the combination of the catalyst (A) with the acid is used, and the amount of the catalyst (A) is 0.1-3% by weight based on the weight of the phenol charged.

7. A process according to Claim 6, wherein the consumption of formaldehyde is 50-95% by weight and the consumption of phenol is 30-75% by weight when the reflux is completed.

8. A process according to Claim 6, wherein the dehydration under reduced pressure after the addition of the acid is effected until the water content in the reaction system becomes not more than 5% by weight.

9. A process according to Claim 6, 7 or 8, wherein the formaldehyde is used in the form of formalin.



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10. A process as claimed in claim 1, carried out substantially as described in any one of Examples Nos. 1 to 6 herein.
11. A phenolic resin whenever prepared by a process as claimed in any one of claims 1 to 10.
12. A shaped structure, comprising a resin as claimed in claim 11 that has been cured.
13. A shaped structure as claimed in claim 12, that is an electrical insulator.

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