We, MONSANTO COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, having its principal place of business at 800 North Lindbergh Boulevard, St. Louis, State of Missouri, United States of America, hereby apply for the grant of a Patent for an invention entitled:

"PROCESS FOR PREPARING HIGH ORTHO NOVOLAC RESINS"

which is described in the accompanying complete specification. This application is a Convention application and is based on an application(s) numbered 758,370 for a patent or similar protection made in United States of America on 10th January 1977.

Our address for service is care of EDWIN F. WELLINGTON, Patent Attorney, 457 St. Kilda Road, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this 6th day of January, A.D. 1978

For and on behalf of MONSANTO COMPANY,

Edwin Wellington
Patent Attorney for Applicant Company

To: The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA.

PROCESS FOR PREPARING HIGH ORTHO NOVOLAC RESINS

BACKGROUND OF THE INVENTION

Conventional novolac resins, prepared from phenolic compounds such as phenol and a source of formaldehyde, in the presence of strong acid catalysts such as sulfuric acid or hydrochloric acid, are used in a variety of applications. These resins have a wide range of properties, including high heat resistance and high mechanical strength, making them suitable for various industrial uses. However, conventional methods of preparation often result in resins with lower performance characteristics, particularly in terms of ortho content and overall reactivity.

The invention described in this application addresses the limitations of conventional novolac resins by proposing a process for preparing high ortho novolac resins. The process involves a novel approach to the reaction conditions, catalyst selection, and reaction parameters, which results in resins with improved ortho content and enhanced performance characteristics. This innovation opens up new possibilities for the application of novolac resins in high-performance consumer products, automotive industries, and electrical components, among others.
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION UNDER Section 11(2) FOR A PATENT OR PATENT OF ADDITION.

In support of the Convention application made under Section 11(2) of the Patents Act 1952 by MONSANTO COMPANY for a patent for an invention entitled

PROCESS FOR PREPARING HIGH ORTHO NOVOLAC RESINS

1. Neal Edmond Willis, International Patent Counsel, Monsanto Company, of 800 North Lindbergh Boulevard, St. Louis, 63166, in the State of Missouri, United States of America, do solemnly and sincerely declare as follows:

1. I am authorized by MONSANTO COMPANY, the applicant for the Patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made at the Patent Office, Washington, District of Columbia, in the United States of America on the 10th of January 1977, by Harry Madison Culbertson.

3. Harry Madison Culbertson, 374 Franklin Street, Belchertown, Massachusetts 01007, United States of America.

is the actual inventor(s) of the invention, and the facts upon which the MONSANTO COMPANY is entitled to make the application are as follows: The Company is the assignee of the actual inventor(s).

4. The basic application referred to in paragraph 2 of this declaration was the first application made in a Convention country in respect of the invention, the subject of the application.

DECLARED at St. Louis, Missouri, aforesaid this 7th day of November, 1977.

NEAL EDMOND WILLIS

To Commissioner of Patents
COMMONWEALTH OF AUSTRALIA

U.S. Patent No. 3,476,707, by H.M. Culbertson has disclosed that in the production of novolac resins, a catalyst system comprising (1) an oxide or hydroxide or organic acid salt of a divalent electropositive metal, and (2) a halogen
Claim 1. A process for the production of phenol-formaldehyde novolac resins which are characterized by having from 75 to 100% of ortho/ortho methylene bridges and prepared by reacting an acid aqueous reaction mixture containing a material selected from the group consisting of phenol and meta-alkylphenols in molar excess with a source of formaldehyde, which process comprises conducting said reacting under aqueous conditions in the presence of a catalyst comprising:

(A) a divalent electropositive metal compound selected from the group consisting of oxides, hydroxides and organic acid salts selected from the group consisting of formates, lactates, acetates, and benzoates, or mixtures thereof, in combination with:

(B) a divalent electropositive metal salt selected from the group consisting of sulfonates, fluoroborates, and mixtures thereof, or

(C) acids selected from the group consisting of sulfonic, fluoroboric, and mixtures thereof,
said reacting being carried out under aqueous reflux conditions, with a phenol to formaldehyde molar ratio of 1.20:1 to 2.0:1, so as to provide said novolac resin with ortho/ortho methylene bridges in an amount of 75 to 100%.
commonwealth of australia

patents act 1952-1969

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complete specification

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jimi

related art:

name of applicant:

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the following statement is a full description of the invention including the best method of performing it known to me/us:

process for preparing high ortho novolac resins

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PROCESS FOR PREPARING HIGH ORTHO NOVOLAC RESINS

BACKGROUND OF THE INVENTION

Conventional novolac resins, prepared from phenolic compounds such as phenol and a source of formaldehyde, in the presence of strong acid catalysts such as sulfuric acid or hydrochloric acid or oxalic acid, are characterized by having a preponderance of para/para and ortho/para methylene bridges as illustrated below:

whereas the so-called “high ortho” novolac resins are characterized by having mostly ortho/ortho methylene bridges as illustrated below:

the main advantage of the “high ortho” novolac resins being the much greater speed of cure when reacted with hexamethylene-tetramine. “High ortho” novolac resins are commonly prepared by reacting phenolic compounds such as phenol and a source of formaldehyde in the presence of either a divalent metal oxide (e.g. MgO and ZnO) or an organic acid salt of a divalent metal (e.g. zinc acetate or magnesium acetate) catalyst system. This invention relates to the production of so-called “high ortho” novolac resins, which are identifiable as being heat-hardenable phenol-formaldehyde resins of enhance hardening speed.
U.S. Patent No. 3,476,707, by H.M. Culbertson, has disclosed that in the production of novolac resins, a catalyst system comprising (1) an oxide or hydroxide or organic acid salt of a divalent electropositive metal, and (2) a halogen acid or halide of a divalent electropositive metal, is particularly effective in promoting "high ortho" orientation in the formation of the resins, with a significant increase in yield and lowering of processing temperature.

Such high ortho novolac resins have ortho orientation of from about 50 to 75% being produced under aqueous conditions.

It has now been discovered that phenol-aldehyde novolac resins can be produced having high ortho orientation of from about 75 to 100% in an improved process. Thus, the invention relates to an improved process for preparing very high ortho novolac resins, said process involving the reaction of phenol and formaldehyde in the presence of a divalent electropositive metal oxide, hydroxide or organic salt, wherein the improvement comprises conducting said reaction under aqueous reflux conditions with said catalysts in combination with a divalent electropositive metal salt selected from the group consisting of sulfonates and fluoroborates or acids selected from the group consisting of sulfonic and fluoroboric or mixtures thereof, as hereinafter described. Such very high ortho novolacs have the technical advance of being heat-hardenable with greatly enhanced hardening rates as bonding resins.

**SUMMARY OF THE INVENTION**

The present invention provides a process for the production of phenol-aldehyde novolac resins which are characterized by having from 75 to 100% of ortho-ortho methylene bridges and prepared by an acid aqueous reaction mixture containing a material selected from the group consisting of phenol and meta-alkylphenols in molar excess with a source of formaldehyde,
which process comprises conducting said reacting under mildly acidic aqueous conditions in the presence of a catalyst comprising:

(A) a divalent electropositive metal compound selected from the group consisting of oxides, hydroxides and organic acid salts selected from the group consisting of formates, lactates, acetates, and benzoates, or mixtures thereof, in combination with:

(B) a divalent electropositive metal salt selected from the group consisting of sulfonates, fluoroborates, and mixtures thereof, or

(C) acids selected from the group consisting of sulfonic, fluoroboric, and mixtures thereof,

said reacting being carried out under aqueous reflux conditions, with a phenol to formaldehyde molar ratio of 1.20:1 to 2.0:1, so as to provide said novolac resin with ortho/ortho methylene bridges in an amount of 75 to 100%.

PREFERRED EMBODIMENTS

DIVALENT ELECTROPOSITIVE METAL COMPOUNDS

Divalent electropositive metals of oxides or hydroxides or organic acid salts employed in accordance with the invention, can be calcium (Ca++), barium (Ba++), strontium (Sr++), magnesium (Mg++), zinc (Zn++), manganous (Mn++) and cobaltous (Co++) cobalt and lead (Pb++). Sulfonic acids employed in accordance with the invention are the aryl sulfonic, e.g., p-toluene, benzene, xylene, phenol and napthalene. Other acids are the alkyl sulfonic, e.g., methane, ethane, trifluoromethane, etc. Acids such as fluoroboric may be used.
The organic acids or organic acid salts of acetic, formic, benzoic and lactic acid may be used in the catalyst system.

An example of a particularly effective catalyst system is a mixture of zinc oxide, manganous acetate and magnesium methane sulfonate (\( \text{Mg(CH}_3\text{SO}_3\text{)}_2 \)). An equally effective alternative is a mixture of zinc oxide, phenolsulfonic acid, manganous acetate and zinc acetate. The catalyst system can comprise the oxide or hydroxide or organic salt and a sulfonate of a different divalent electropositive metal. Typical organic acid salts useful in the catalyst system are calcium formate, zinc acetate, magnesium acetate, manganous acetate, lead acetate and zinc benzoate. The magnesium organic acid salts, such as the magnesium sulfanates, have been found to be particularly effective when used in combination with zinc oxide. Generally, the preferred catalyst system comprises the sulfonates and/or sulfonic acids in combination with zinc oxide.

The effectiveness of the catalyst system according to the invention varies with respect to solubility limitations of the oxides or hydroxides or salts and the sulfonates and with respect to their ability to direct the condensation of the formaldehyde with the phenol or meta-alkylphenol, the relative amount of (1) oxide or hydroxide or salt, and (2) sulfonic acid or sulfonate as well as the total amount employed, varying according to solubility and the necessity to maintain the pH in the pH 4 to pH 7 range. In general, the amount of oxide or
The catalyst system can comprise a sulfonic acid, such as acetic, and a sulfonate, such as calcium acetate, or salt, calculated as percentage based on the amount of phenol or meta-alkylphenol, is within the range of 0.1 to 2.0%, the preferred amount being within 0.2 to 0.5%; in general the amount of sulfonate, calculated as percentage based on the amount of phenol or meta-alkylphenol, is within the range of 0.05 to 2.0%, the preferred amount being within 0.1 to 1.0%; and in general the amount of sulfonic acid, calculated as percentage (100% acid) based on the amount of phenol or meta-alkylphenol, is within the range of 0.02 to 1.0%, the preferred amount being within 0.05 to 0.25%.

Meta-alkylphenols as well as phenol, form fast-curing novolac resins when reacted with a source of formaldehyde in accordance with the invention, the phenol and meta-alkylphenol materials including the commercial materials commonly used for the production of such resins. The source of formaldehyde includes conventional formalin solutions for the purpose, as well as materials such as paraformaldehyde, which produce formaldehyde under the conditions of the condensation reaction. The molar ratio of phenol to formaldehyde generally lies between 1.20:1 and 2:1, the preferred range being 1.25:1 to 1.45:1. The excess is kept above 1.20:1 in order to prevent gelation and is generally below 2:1 for economic reasons, another factor influencing the choice of molar excess being the molecular weight range generally desired for the resin.

Preparation of "high ortho" novolac resins in accordance with the invention is seen to be essentially a three stage process, the first stage being the formation of methylol derivatives as illustrated by the following:
The amount of phenol \( \text{CH}_2\text{OH} \) used, as well as the curing agent for the phenol, is important in the condensation process. The ratio of formaldehyde to phenol is usually between 1:0.5 and 1.0%, and the phenol is primarily used in the form of a formaldehyde phenol hydrate. The ratio of formaldehyde to phenol is significant in the curing process.

In the first stage of the reaction, the formation of benzyl ethers takes place. This involves the condensation of free methylols, as illustrated by the following equation:

\[
\text{O} + \text{CH}_2\text{O} \xrightarrow{\text{oxide/hydroxide/salt}} \text{OH-CH}_2\text{O-CH}_2\text{OH}
\]

wherein \( X \) is \( \text{CH}_2\text{OH} \). With the presence of the divalent oxides at pH of pH 4-7, orientation of methylols is predominantly ortho (structures I and II), whereas at pH greater than pH 7, the amount of para substitution increases and an appreciable amount of trimethylol (structure V) derivative is formed. In the second stage, the formation of benzyl ethers takes place as illustrated by the following:

\[
\text{OH-CH}_2\text{OH} + \text{H}^+ \xrightarrow{} \text{OH-CH}_2\text{O-CH}_2\text{OH}
\]

wherein \( X \) is \( \text{CH}_2\text{OH} \), this reaction taking place only under mildly acidic conditions (pH 4 up to pH 7). In the third stage, the formation of methylene bridges takes place through the breaking down of the benzyl ether and reaction with excess phenol which is present, and the condensation of free methylols, as illustrated by the following:
and I consider that it is in the third stage that the divalent metal sulfonate or sulfonic acid effects a particularly valuable function. The stability of the benzyl ethers is quite pronounced, thus when the prior art organic acid salts or oxides are employed alone, which materials probably are present in the form of the phenate salts, temperatures of up to 160°C. are required. On the other hand, we have found that the presence of the sulfonate or sulfonic acid catalyzes the decomposition of the benzyl ethers at temperatures as low as 115°C. The pH range specified above is critical in this reaction, since if greater than pH 7, a base-catalyzed condensation takes place, with poor control of orientation and possible gelation at the lower phenol/formaldehyde ratios, whereas if the pH is below pH 4, the orientation is predominantly para, with subsequent loss of reactivity of the resin.

The relation of the above sequence of reactions to the actual processing steps described in the practical examples can be summarized as follows: Stage 1 (methylation)—initial 3 hours reflux; Stage 2 (ether formation)—dehydration to 125°C. and Stage 3 (condensation)—reflux at 125°C., in all cases a mixture of oxide or hydroxide or salt and sulfonate being
present whether the sulfonate is added in the form of the metal sulfonate or the sulfonic acid. The role of the metal oxide or hydroxide or salt in the catalyst system is therefore seen to be (1) control of pH in the presence of the strong acids, and (2) increase in the concentration of metal ions which catalyze the initial stage (methylolation) of the reaction and control orientation in the initial and subsequent reaction stages. The role of the sulfonate is seen to (1) increase in the concentration of metal ions, as above, and most importantly, (2) catalyze the decomposition of the intermediate ether at much lower temperatures.

These novolacs have a total ortho orientation of 75 to 100% which distinguishes them from conventional high ortho novolacs which have an ortho orientation of 50-75%. The very high ortho orientation results in a much more linear polymer with unusual and valuable properties.

Synthesis of these novolacs can thus be readily 50

The following examples are illustrative only and are not intended to limit the scope of the invention.
The claims defining the invention are as follows:

1. A process for the production of phenol-formaldehyde novolac resins which are characterized by having from 75 to 100% of ortho/ortho methylene bridges and prepared by reacting an acid aqueous reaction mixture containing a material selected from the group consisting of phenol and meta-alkylphenols in molar excess with a source of formaldehyde, which process comprises conducting said reacting under mildly acidic aqueous conditions in the presence of a catalyst comprising:

   (A) a divalent electropositive metal compound selected from the group consisting of oxides, hydroxides and organic acid salts selected from the group consisting of formates, lactates, acetates, and benzoates, or mixtures thereof, in combination with:

   (B) a divalent electropositive metal salt selected from the group consisting of sultonates, fluoroborates, and mixtures thereof, or

   (C) acids selected from the group consisting of sulfonic, fluoroboric, and mixtures thereof,

   said reacting being carried out under aqueous reflux conditions, with a phenol to formaldehyde molar ratio of 1.20:1 to 2.0:1, so as to provide said novolac resin with ortho/ortho methylene bridges in an amount of 75 to 100%.

2. A process of claim 1 wherein said catalyst component (A) is used in combination with sulfonic or fluoroboric acid.

3. A process of claim 1 wherein said catalyst component (A) is used in combination with a divalent metal sulfonate or fluoroborate salt.
formaldehyde from 75 to 95% by reacting a material selected from the group of p-alkylphenols in an acidic aqueous solution containing:

- divalent electropositive metal of catalyst component is magnesium (Mg++) or zinc (Zn++), or manganous (Mn++) or calcium (Ca++), or barium (Ba++), or cobaltous (Co++) or lead (Pb++).}

5. A process of claim 4 wherein said divalent electropositive metal of catalyst component (A) is magnesium (Mg++), zinc (Zn++) or manganous (Mn++).

6. A process of any one of claims 1 to 5 wherein the amount of said catalyst component (A) is in the range of 0.1 to 2.0% by weight, the amount of said acids are within the range of 0.05 to 1.0% by weight, or the amount of said sulfonate and fluoroborate salts are in the range of from 0.2 to 1.0% by weight, each based on the weight of phenol or meta-alkylphenol.

7. A process of any one of claims 1 to 6 wherein said reacting is conducted in the presence of greater than 5% by weight of water based on said reaction mixture.

8. A process of claim 7 wherein said water is present in amounts of from 6 to 50% by weight based on said reaction mixture.

9. A high-ortho phenol-formaldehyde novolac resin prepared by the process of any one of claims 1 to 8.

DATED this 21st day of May, A.D. 1981