



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>C08L 61/06</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/16827</b> (43) International Publication Date: 8 April 1999 (08.04.99)</p>
<p>(21) International Application Number: PCT/US98/19889 (22) International Filing Date: 29 September 1998 (29.09.98) (30) Priority Data: 08/942,061 1 October 1997 (01.10.97) US (71) Applicant: HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US). (72) Inventors: MCCORMICK, David, R.; 1326 West Selfridge, Clawson, MI 48017 (US). LINDERT, Andreas; 5409 Patterson, Troy, MI 48098 (US). PIERCE, John, R.; 1312 Winchester, Huntington Woods, MI 48070 (US). (74) Agent: MILLSON, Henry, E.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: PROCESS AND COMPOSITIONS CONTAINING POLYPHENOL COPOLYMERS</p>		
<p>(57) Abstract</p> <p>Processes for the preparation of polyphenol polymers useful as surface coatings wherein the process is carried out in the absence of organic solvents, and the polyphenol polymers are the reaction products of a phenolic polymer or copolymer, an amine, and an aldehyde, ketone, or mixture thereof; and the aqueous solutions resulting therefrom.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## PROCESS AND COMPOSITIONS CONTAINING POLYPHENOL COPOLYMERS

### Background of the Invention

#### 1. Field of the Invention

This invention relates to aqueous solutions of polyphenol polymers useful as surface coatings, and to methods for their preparation.

#### 2. Statement of Related Art

Compositions for the treatment of surfaces with derivatives of polyphenol compounds are known.

However, such phenolic compounds are all prepared in the presence of one or more organic solvents, and the resulting solutions or dispersions are, after optional dilution with water, used without the removal of the organic solvent component.

### DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

It has now been discovered that aqueous solutions of polyphenol polymers can be prepared in the absence of organic solvents, and that the resulting aqueous solutions exhibit surprising improvements over prior organic solvent containing compositions, including aqueous compositions containing organic solvents. These improvements include enhanced cold and warm

weather stability, elimination of solvent odor and hazardous flash points, reduced foaming during use, lower reaction temperatures, lower residual amine, easier low molecular weight cation removal, and increased yield of desired reaction products which results in lower residual formaldehyde concentrations and other  
5 volatile organic compounds.

The aqueous solutions of the polyphenol polymers produced by the process of the invention are the reaction products of

- A) at least one phenolic polymer or copolymer;
- B) an aldehyde, ketone, or mixture thereof; and
- 10 C) at least one amine.

The process of the invention comprises the following steps:

- I) reacting the phenolic polymer or copolymer (component A) in water with an organic or inorganic base to form the corresponding phenoxide salt;
- 15 II) reacting the aqueous solution from step I) with the amine, which is preferably a secondary amine (component C) and the aldehyde, ketone, or mixture thereof (component B) at a temperature in the range of from 20° to 100° C., preferably from 50° to 80° C.;
- 20 III) adding an acid to neutralize the base and to react with the amine functionality in the product to solubilize the product; and
- IV) passing the resulting aqueous solution from step III) through an acid cation exchange column (H<sup>+</sup> form) to remove base ions, such as sodium ions. If it is desired to also remove unreacted secondary amine

as well, a strong acid cation exchange column is used. If it is desired to remove only base ions, a weak acid cation exchange column is used.

The quantities of components A), B) and C) used to prepare the polyphenol polymer product in aqueous solution are generally from about 0.25 to about 2.0 molecular equivalents of component B), and from about 0.25 to about 2.0 molecular equivalents of component C), based on 1 molecular equivalent of component A. The absolute quantities of these components are selected to provide an aqueous solution from step IV) that contains from 5 to 50, preferably from 15 to 35% by weight of solids in the solution. Viscosity considerations will of course determine the upper concentration of any particular product.

In step I) the organic or inorganic base is preferably an alkali metal hydroxide, e.g. sodium or potassium hydroxide, although tetraalkylammonium hydroxides, e.g. tetrabutylammonium hydroxide, or tetraaryl ammonium hydroxides can also be used. The base should be present in at least 10 mole %, and preferably at least 25 mole%, based on the phenolic polymer or copolymer.

Step I) is preferably carried out at a temperature in the range of from 20° to 50° C., more preferably from 20° to 25° C.

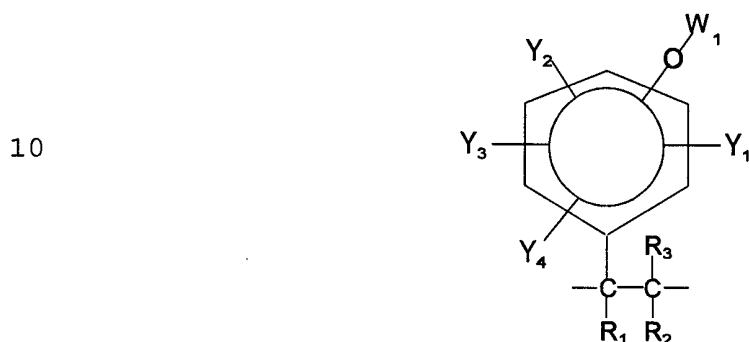
In step III) the acid used to neutralize the base can be organic or inorganic. Useful and preferred acids for this purpose include carbonic acid, acetic acid, citric acid, oxalic acid, ascorbic acid, phenylphosphonic acid, chloromethylphosphonic acid; mono, di and trichloroacetic acid, trifluoroacetic

acid, nitric acid, phosphoric acid, hydrofluoric acid, sulfuric acid, boric acid, hydrochloric acid, and the like; these may be employed alone or in combination with each other. The most preferred acid is phosphoric acid.

In step IV), strong acid cation exchange columns are those of the sulfonic acid or phosphonic acid types. Weak acid cation exchange columns are those of the carboxylic acid type.

Component A), i.e. the phenolic polymer or copolymer, is preferably selected from the following polymeric compounds:

- a) a polymer material having at least one unit having the formula:



where;

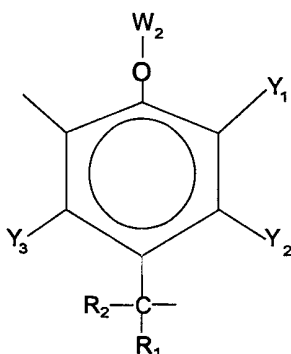
R<sub>1</sub> through R<sub>3</sub> are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, or an aryl group having about 6 to about 18 carbon atoms;

15

Y<sub>1</sub> through Y<sub>4</sub> are independently selected for each of said units from the group consisting of hydrogen, or an alkyl or aryl group having from 1 to 18 carbon atoms; and

$W_1$  is independently selected for each of said units from hydrogen or a hydrolyzable group such as an acyl group, e.g. acetyl, benzoyl, and the like. Hydrogen is preferred.

b) a polymer material having at least one unit having the formula:



5 wherein;

$R_1$  through  $R_2$  are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, or an aryl group having from about 6 to about 18 carbon atoms;

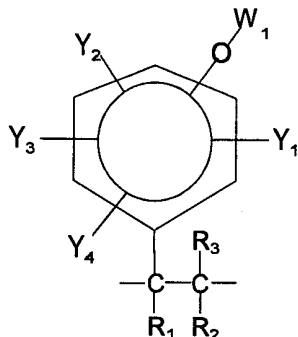
10  $Y_1$  through  $Y_3$  are independently selected for each of said units from the group consisting of hydrogen or an alkyl or aryl group having from 1 to 18 carbon atoms; and

$W_1$  is independently selected for each of said units from hydrogen or a hydrolyzable group such as an acyl group, e.g. acetyl, benzoyl, and the like. Hydrogen is preferred.

15

c) a copolymer material wherein at least one portion of said co-

polymer has the structure:



and at least a fraction of said portion is polymerized with one or more monomers having a C=C moiety. Useful monomers include those independently selected for each of said units from the group consisting of acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide, n-amyl methacrylate, styrene, m-bromostyrene, p-bromostyrene, pyridine, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, tert-butylamino-ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, n-butyl vinyl ether, tert-butyl vinyl ether, m-chlorostyrene, o-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-diallylmelamine, N,N-di-n-butylacrylamide, di-n-butyl itaconate, di-n-butyl maleate, diethylaminoethyl methacrylate, diethyleneglycol monovinyl ether, diethyl fumarate, diethyl itaconate, diethyl vinylphosphonate, vinylphosphonic acid, diisobutyl maleate, diisopropyl itaconate,

diisopropyl maleate, dimethyl fumarate, dimethyl itaconate, dimethyl maleate, di-n-nonyl fumarate, di-n-nonyl maleate, dioctyl fumarate, di-n-octyl itaconate, di-n-propyl itaconate, n-dodecyl vinyl ether, ethyl acid fumarate, ethyl acid maleate, ethyl acrylate, ethyl cinnamate, N-ethylmethacrylamide, ethyl methacrylate, ethyl vinyl ether, 5-ethyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine-1-oxide, glycidyl acrylate, glycidyl methacrylate, n-hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, isobutyl methacrylate, isobutyl vinyl ether, isoprene, isopropyl methacrylate, isopropyl vinyl ether, itaconic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylolmethacrylamide, N-isobutoxymethylacrylamide, N-isobutoxymethylmethacrylamide, N-alkyloxymethylacrylamide, N-alkyloxymethylmethacrylamide, N-vinylcaprolactam, methyl acrylate, N-methylmethacrylamide,  $\alpha$ -methylstyrene, m-methylstyrene, o-methylstyrene, p-methylstyrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium p-styrenesulfonate, stearyl methacrylate, styrene, p-styrene-sulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinylcarbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridine, 2-vinylpyridine N-oxide, 4-vinylpyrimidine, N-vinylpyrrolidone; and  $W_1$ ,  $Y_1$ - $Y_4$  and  $R_1$ - $R_3$  are as in (a), above.

Within such materials, the ratio of any single monomer to any other monomer can be about 1:99 to about 99:1, preferably about 5:1 to about

1:5, and more preferably 1.5:1 to about 1:1.5.

d) a condensation polymer, i.e. wherein any of polymeric materials a), b) or c) is condensed with a second compound selected from the group consisting of phenols (preferably phenol, alkylphenol, arylphenol, cresol, resorcinol, catechol, pyrogallol), tannins, (both hydrolyzable and condensed) novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce a condensation resin product.

The molecular weight of component A can be in the range of 360 to 30,000 or greater. Preferred component A is poly (4-vinylphenol) having a molecular weight of from 2500 to 10,000, preferably around 5,000.

The term "copolymer" used herein includes polymers, such as terpolymers, made up of two or more monomer components.

Component B) is preferably an aldehyde, and most preferably is formaldehyde, especially in the form of paraformaldehyde. Formaldehyde is generally commercially available in a form that contains a significant quantity of methanol, e.g. 15% methanol. Since the present process is carried out in the absence of organic solvents, formaldehyde free from methanol should be used, such as uninhibited aqueous formaldehyde. Paraformaldehyde is also a convenient form of formaldehyde that does not contain any alcohol component.

Component C) is an amine, preferably a secondary amine, e.g. methylethylamine, dimethylamine, diethylamine, diethanolamine, dipropylamine, di-n-butylamine, diisoamylamine, dibenzylamine, methyldiethylethylenediamine, methylaniline, piperidine, 1,2,3,4- tetrahydroisoquinoline, 6-methoxy-1,2,3,4-

tetrahydroisoquinoline, morpholine, piperazine,  $\alpha$ -methylaminopropiophenone,  $\alpha$ -acetylethylbenzylamine; benzyl-(2-cyclohexanonylmethyl)-amine, 3,4-methylenedioxybenzyl-(2-cyclohexanonylmethyl)-amine, N-methyl-glucamine, glucosamine, and t-butylamine; or mixtures thereof. Primary amines can also  
5 be used, such as C<sub>1</sub>-C<sub>12</sub> alkyl amines and the like.

An optional further step V) can be employed if it is desired to add a fluorometallic acid to the composition. Step V) is carried out by adding to the composition from step IV) a fluorometallic acid, e.g. fluorotitanic acid (H<sub>2</sub> Ti F<sub>6</sub>), fluorosilic acid (H<sub>2</sub> Si F<sub>6</sub>), fluorozirconic acid (H<sub>2</sub> Zr F<sub>6</sub>), and the like, generally in  
10 from about 0.01 to about 5.0% by weight, based on the weight of the final aqueous composition. The solution can then again be passed through an acid cation exchange column.

Alternatively, instead of step V), the acid used in step III) can be a fluorometallic acid.

15 The compositions and processes of the present invention are useful in treating a broad range of metal surfaces, including metals having surfaces that have been conversion coated with suitable conversion coatings such as iron phosphate, manganese phosphate, zinc phosphate, and zinc phosphate modified with calcium, nickel, or manganese ions. Examples of suitable metal  
20 surfaces include zinc, iron, aluminum and cold-rolled, polished, pickled, and hot-rolled steel and galvanized steel surfaces. As used herein, the term "metal surface" includes both untreated metal surfaces and conversion coated metal surfaces. With regard to aluminum surfaces, the compositions and methods of

the present invention can be applied prior to or in place of, any additional corrosion-resistance/paint-based surface treatments.

The compositions and processes of the invention can also be used to treat plastic and "plastic-like" surfaces. Preferred plastic and "plastic-like" surfaces include the surfaces of resins and polymeric materials, including thermoplastic and thermosetting polymers, as well as natural rubbers, mixtures of these materials, and the like.

The aqueous compositions of the invention can be diluted with water to a solids content of from 0.001% to 20% by weight, with a solids content of from 0.001 to 5% by weight being preferred.

The thickness of the dry coating will depend on its purpose or function, but typically ranges from about 0.0001 mil to 25 mils or greater.

The invention will be illustrated but not limited by the following examples.

### EXAMPLES

Example 1:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 353.5g of deionized water, 4.7 grams of sodium hydroxide and 32.3g of methylethanolamine were added and mixed till dissolved. 53.8g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 13.9g

of 92% paraformaldehyde was added with continued mixing. The solution was mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 65° C. and held for 1.5 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml  
5 beaker equipped with a stirrer, and diluted with 508.4 grams of deionized water. The solution was mixed and 33.4g of 75% phosphoric acid was added. After adding the phosphoric acid the solution went from clear to very turbid and then cleared up again within one hour. The pH at this stage was 6.7. The solution was then passed through an ion-exchange column containing at least 100ml of  
10 Rohm and Haas IR-120+ cation exchange resin. The final pH was 5.4. The sodium level was less than 1ppm and the residual formaldehyde was 90ppm. 3.33g of 60% fluotitanic acid and 107.8g of deionized water were then added with mixing.

#### Example 2:

15 To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 353.5g of deionized water, 4.7 grams of sodium hydroxide and 32.3g of methylethanolamine were added and mixed till dissolved. 53.8g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to  
20 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30°C. and 13.9g of 92% paraformaldehyde was added with continued mixing. The solution was

mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 65° C. and held for 1.5 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 616.2 grams of deionized water.

5 The solution was mixed and 33.4g of 75% phosphoric acid was added. After adding the phosphoric acid the solution went from clear to very turbid and then cleared up again within one hour. The pH at this stage was 6.7. The solution was then recirculated through an ion-exchange column containing at least 100ml of Rohm and Haas IR-120+ cation exchange resin until the pH was less than

10 6.25. 3.33g of 60% fluotitanic acid was then added with mixing. The solution was then passed through the same cation exchange column. The final pH was 4.9, the sodium level was <1ppm and the residual formaldehyde was 81ppm. No titanium was removed during the deionization step.

### Example 3:

15 To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 196.71g of deionized water, 2.98 grams of sodium hydroxide and 59.34g of N-methyl-D-glucamine were added and mixed till dissolved. 35.76g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to

20 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 9.73g of 92% paraformaldehyde was added with continued mixing. The solution was

mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 75° C. and held for 10 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 678.74 grams of deionized water.

5 The solution was mixed and 16.74g of 75% phosphoric acid was added with mixing. The pH at this point was 7.3. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 5.5. The sodium level was less than 1ppm and the residual formaldehyde was 300ppm.

10 Example 4:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 196.71g of deionized water, 2.98 grams of sodium hydroxide and 59.34g of N-methyl-D-glucamine were added and mixed till dissolved. 35.76g of poly(4-  
15 hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 9.73g of 92% paraformaldehyde was added with continued mixing. The solution was mixed for 30 minutes after which the paraformaldehyde was completely  
20 dissolved. The solution was then heated with mixing to 75° C. and held for 10 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 587.41 grams of deionized water.

The solution was mixed and 108.07g of 20% fluozirconic acid was added with mixing. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 3.5. The sodium level was less than 1ppm and the residual  
5 formaldehyde was 300ppm.

#### Example 5:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 353.5g of deionized water, 4.7 grams of sodium hydroxide and 32.3g of  
10 methylethanolamine were added and mixed till dissolved. 53.8g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 13.9g of 92% paraformaldehyde was added with continued mixing. The solution was  
15 mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 65° C. and held for 1.5 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 508.4 grams of deionized water. The solution was mixed and 33.4g of 75% phosphoric acid was added. After  
20 adding the phosphoric acid the solution went from clear to very turbid and then cleared up again within one hour. The pH at this stage was 6.7. The solution was then passed through an ion-exchange column containing at least 100ml of

Rohm and Haas IR-120+ cation exchange resin. The final pH was 5.4. The sodium level was less than 1ppm and the residual formaldehyde was 90ppm.

Example 6:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer,  
5 reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 353.5g  
of deionized water, 4.7 grams of sodium hydroxide and 23.8g of  
methylethanolamine were added and mixed till dissolved. 53.8g of poly(4-  
hydroxystyrene) was then added with mixing. The mixture was then heated to  
65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was  
10 completely dissolved. The solution was then allowed to cool to 30°C. and 10.2g  
of 92% paraformaldehyde was added with continued mixing. The solution was  
mixed for 30 minutes after which the paraformaldehyde was completely  
dissolved. The solution was then heated with mixing to 65° C. and held for 1.5  
hours. After the solution cooled to about 30° C. it was transferred to a 1500ml  
15 beaker equipped with a stirrer, and diluted with 512.6 grams of deionized water.  
The solution was mixed and 41.4g of 75% phosphoric acid was added. After  
adding the phosphoric acid the solution went from clear to very turbid and then  
cleared up again within one hour. The pH at this stage was 4.75. The solution  
was then passed through an ion-exchange column containing at least 100ml of  
20 Rohm and Haas IR-120+ cation exchange resin. The final pH was 2.25. The  
sodium level was less than 1ppm and the residual formaldehyde was  
<50ppm.

## Example 7:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 196.71g of deionized water, 2.98 grams of sodium hydroxide and 59.34g of N-methyl-D-glucamine were added and mixed till dissolved. 35.76g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 9.73g of 92% paraformaldehyde was added with continued mixing. The solution was mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 75° C. and held for 10 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 675.13 grams of deionized water. The solution was mixed and 20.35g of 60% fluotitanic acid was added with mixing. The pH at this stage was 6.7. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 4.65. The sodium level was less than 1ppm and the residual formaldehyde was 300ppm.

## Example 8:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 196.71g of deionized water, 2.98 grams of sodium hydroxide and 59.34g of N-methyl-D-

glucamine were added and mixed till dissolved. 35.76g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 9.73g  
5 of 92% paraformaldehyde was added with continued mixing. The solution was mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 75° C. and held for 10 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml beaker equipped with a stirrer, and diluted with 682.33 grams of deionized water.  
10 The solution was mixed and 13.15g of 70% nitric acid was added with mixing. The pH at this stage was 8.25. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 6.19. The sodium level was less than 1ppm and the residual formaldehyde was 300ppm.

15 Example 9:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 196.71g of deionized water, 2.98 grams of sodium hydroxide and 59.34g of N-methyl-D-glucamine were added and mixed till dissolved. 35.76g of poly(4-  
20 hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 9.73g

of 92% paraformaldehyde was added with continued mixing. The solution was mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 75° C. and held for 10 hours. After the solution cooled to about 30° C. it was transferred to a 1500ml  
5 beaker equipped with a stirrer, and diluted with 685.45 grams of deionized water. The solution was mixed and 10.03g of 98% sulfuric acid was added with mixing. The pH at this stage was 7.47. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 5.43. The sodium level was less than 1ppm  
10 and the residual formaldehyde was 300ppm.

#### Example 10:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 320.10g of deionized water, 4.48 grams of sodium hydroxide and 38.14g of  
15 ethylethanolamine were added and mixed till dissolved. 51.33g of poly(4-hydroxystyrene) was then added with mixing. The mixture was then heated to 65° C. with mixing. After 1.5 hours of mixing at 65° C. the polymer was completely dissolved. The solution was then allowed to cool to 30° C. and 13.96g of 92% paraformaldehyde was added with continued mixing. The  
20 solution was mixed for 30 minutes after which the paraformaldehyde was completely dissolved. The solution was then heated with mixing to 70° C. and held for 4 hours. After the solution cooled to about 30° C. it was transferred to

a 1500ml beaker equipped with a stirrer, and diluted with 538.45 grams of deionized water. The solution was mixed and 33.54g of 75% phosphoric acid was added with mixing. The pH at this stage was 6.75. The solution was then passed through an ion-exchange column containing at least 150ml of Rohm and Haas IR-120+ cation exchange resin. The final pH was 4.5. The sodium level was less than 1ppm and the residual formaldehyde was 900ppm.

#### Comparison Example C1:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 94.59g of propoxypropanol was added. 53.29g of poly(4-hydroxystyrene) was then slowly added with mixing. The solution was then heated with mixing to 80° C. and held for 1 hour after which the polymer was completely dissolved. The solution was then cooled to 45°C. and 33.29g of methylethanolamine was added followed by 106.47g deionized water with continued mixing. 36.00g of 37% formaldehyde solution (contained 10% methanol inhibitor) was added slowly over a period of 45 minutes with continued mixing while the temperature was maintained at 45° - 50° C. After the formaldehyde addition, the solution was held at 45° - 50° C. for two additional hours and then heated to and maintained at 80° C. for three hours. The solution was then cooled to 30° C and 14.47g of 75% phosphoric acid was added and mixed well. The solution was then transferred to a 1500ml beaker equipped with a stirrer. 661.89g of deionized water was then added with mixing. The resulting solution had a residual formaldehyde level of

800ppm. The final pH was 7.43.

#### Comparison Example C2:

To a 500ml 3-neck round bottom flask equipped with an overhead stirrer, reflux condenser, nitrogen gas inlet, heating mantle and thermocouple, 83.33g of n-propoxypropanol was added. 37.58g of poly(4-hydroxystyrene) was then slowly added with mixing. The solution was then heated with mixing to 80° C. and held for 1 hour after which the polymer was completely dissolved. The solution was then cooled to 45° C. and a solution of 61.88g of N-methyl-D-glucamine in 93.75g deionized water was added with continued mixing. The solution was heated to 57°C. and with continued mixing 25.42g of 37% formaldehyde (contained 10% methanol inhibitor) was added slowly over a period of 45 minutes. After the formaldehyde addition, the solution was heated to and maintained at 90°C. for nine hours. The solution was then cooled to 30° C. and transferred to a 1500ml beaker equipped with a stirrer. 693.88g of deionized water was then added with mixing followed by 4.17g of 75% phosphoric acid. The resulting solution had a residual formaldehyde level of 650ppm. The final pH was 8.1.

#### Example 11:

The properties of the composition of Example 3 were compared to the properties of the composition of Comparative Example 2, and the results are set forth in Table 1 below:

TABLE 1

Property	<u>Example 3</u>	<u>Comparative Example 2</u>
pH	5.5	8.2
% polymer	8.50	8.50
5 % phosphoric acid	1.26	0.32
Residual CH <sub>2</sub> O	200-300ppm	650ppm
Volatile organic compounds	<0.1% wt/wt	8.58% wt/wt
Oxidizable compounds	177,500ppm	410,000ppm
stability @ 49° C.	30 days	30 days
10 freezing point	-11° C.	-1° C.
cold stability	> -11° C.	> 4.5° C.
flash point	> 93° C.	61° C.

Example 12

The properties of the composition of Example 5 were compared to the properties of the composition of Comparative Example 1, and the results are set forth in Table 2 below:

TABLE 2

Property	<u>Example 5</u>	<u>Comparative Example 1</u>
pH	5.50	7.25
20 % polymer	9.2	9.2
% phosphoric acid	2.50	1.08
Residual CH <sub>2</sub> O	<100ppm	800ppm
Volatile organic compounds	<0.1% wt/wt	9.98% wt/wt
Oxidizable compounds	250,000ppm	520,000ppm
25 stability @ 49° C.	55 days	5 days
freezing point	-11° C.	-1° C.
cold stability	> -11° C.	> 4.5° C.
flash point	> 93° C.	59° C.

Example 13:

Foaming studies were carried out comparing the foam heights of 1% aqueous solutions of the compositions of Example 3 and Comparison Example 2, and 1% aqueous solutions of the compositions of Example 5 and Comparison Example 1. Each aqueous solution also contained 5ppm of Parker Amchem Pln 95B defoamer. The solutions were sprayed at 5 psi at 120° F. on identical conversion coated metal surfaces at the rate of 2 sq. ft./liter. The results are given in Tables 3 and 4 below:

TABLE 3

EXAMPLE	FOAM HEIGHT (cm) <sup>1</sup>	FOAM HEIGHT (cm) <sup>2</sup>
3	0.1	0.2
C2	1.0	1.5

1 - 1% aqueous solutions prepared with Detroit tap water

2 - 1% aqueous solutions prepared with hard well water

TABLE 4

EXAMPLE	FOAM HEIGHT (cm) <sup>1</sup>	FOAM HEIGHT (cm) <sup>2</sup>
5	0.2	2.0
C1	1.0	9.0

1 - 1% aqueous solutions prepared with Detroit tap water

2 - 1% aqueous solutions prepared with hard well water

What is claimed is:

1. A process for the preparation of aqueous solutions of resins comprising a phenolic polymer, formaldehyde, and a secondary amine comprising the steps of:

- I) reacting at least one phenolic polymer or copolymer in water with an organic or inorganic base to form the corresponding phenoxide salt;
- II) reacting the aqueous solution from step I) with at least one primary or secondary amine and with an aldehyde, ketone, or mixture thereof at a temperature in the range of from about 20° to about 100° C.;
- III) adding at least one acid to the reaction mixture from step II) to neutralize any remaining organic or inorganic base and to react with amine functionality in the product to solubilize the product; and
- IV) passing the resulting aqueous solution from step III) through an acid cation exchange column (H<sup>+</sup> form);

wherein the process is carried out in the absence of organic solvents, and the aqueous solution obtained from the process is free from organic solvents and does not contain 0.18% fluorotitanic acid.

2. The process of claim 1 wherein in step I) the phenolic polymer or copolymer is polyvinylphenol.
3. The process of claim 1 wherein in step I) the organic or inorganic base is an alkali metal hydroxide.
4. The process of claim 3 wherein the base is sodium hydroxide.
5. The process of claim 1 wherein step I) is carried out at a temperature in

the range of from about 20° to about 50° C.

6. The process of claim 1 wherein in step II) the at least one amine is at least one secondary amine selected from the group consisting of N-methylethanolamine, methylethylamine, dimethylamine, diethylamine, diethanolamine, dipropylamine, di-n-butylamine, diisoamylamine, dibenzylamine, methyldiethylethylenediamine, methylaniline, piperidine, 1,2,3,4-tetrahydroisoquinoline, 6-methoxy-1,2,3,4-tetrahydroisoquinoline, morpholine, piperazine,  $\alpha$ -methylaminopropiophenone,  $\alpha$ -acetylethylbenzylamine; benzyl-(2-cyclohexanonylmethyl)-amine, 3,4-methylenedioxybenzyl-(2-cyclohexanonylmethyl)-amine, N-methyl-glucamine, glucosamine, and t-butylamine.

7. The process of claim 1 wherein in step II) the aldehyde, ketone or mixture thereof is anhydrous formaldehyde, aqueous formaldehyde, or paraformaldehyde.

8. The process of claim 1 wherein the at least one acid in step III) is selected from the group consisting of carbonic acid, acetic acid, citric acid, oxalic acid ascorbic acid, phenylphosphonic acid, chloromethylphosphonic acid; mono, di and trichloroacetic acid, trifluoroacetic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulfuric acid, boric acid, and hydrochloric acid.

9. The process of claim 8 wherein the at least one acid is phosphoric acid.

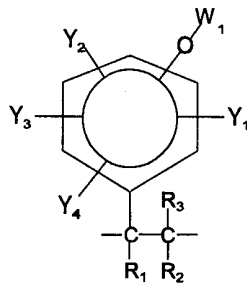
10. The process of claim 1 wherein in step IV) the acid cation exchange column is a strong acid cation exchange column.

11. The process of claim 1 wherein in step IV) the acid cation exchange

column is a weak acid cation exchange column.

12. The process of claim 1 wherein in step I) the at least one phenolic polymer or copolymer is selected from the group consisting of

a) a polymer material having at least one unit having the formula:



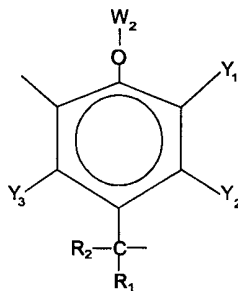
where;

$R_1$  through  $R_3$  are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, and an aryl group having about 6 to about 18 carbon atoms;

$Y_1$  through  $Y_4$  are independently selected for each of said units from the group consisting of hydrogen, and an alkyl or aryl group having from 1 to 18 carbon atoms;

$W_1$  is independently selected for each of said units from hydrogen or a hydrolyzable group;

b) a polymer material having at least one unit having the formula:



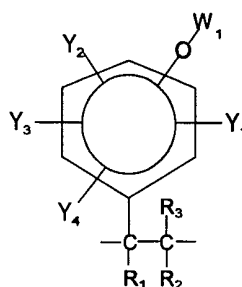
wherein;

$R_1$  through  $R_2$  are independently selected for each of said units from the group consisting of hydrogen, an alkyl group having from 1 to about 5 carbon atoms, and an aryl group having from about 6 to about 18 carbon atoms;

$Y_1$  through  $Y_3$  are independently selected for each of said units from the group consisting of hydrogen and an alkyl or aryl group having from 1 to 18 carbon atoms.

$W_1$  is independently selected for each of said units from hydrogen or a hydrolyzable group;

c) a copolymer material wherein at least one portion of said copolymer has the structure:



wherein  $Y_1$ - $Y_4$ ,  $R_1$ - $R_3$  and  $W_1$  are as defined above and at least a fraction of said portion is polymerized with one or more monomers having a C=C moiety; and

d) a condensation polymer wherein any of polymer materials a), b) or c) is condensed with a second compound selected from the group consisting of phenols, tannins, novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce the condensation polymers.

13. The process of claim 1 wherein in step I) the phenolic polymer or copolymer is polyvinylphenol and the base is an alkali metal hydroxide; in step II) the aldehyde, ketone, or mixture thereof is anhydrous formaldehyde or paraformaldehyde; and in step III the at least one acid is phosphoric acid.

14. The process of claim 13 wherein in step IV) the acid cation exchange column is a strong acid cation exchange column.

15. The process of claim 1 for the preparation of aqueous solutions of resins comprising a phenolic polymer, formaldehyde, and a primary or secondary amine comprising the steps of:

- I) reacting at least one phenolic polymer or copolymer in water with an organic or inorganic base to form the corresponding phenoxide salt;
- II) reacting the aqueous solution from step I) with at least one secondary amine and with an aldehyde, ketone, or mixture thereof at a temperature in the range of from about 20° to about 100° C.;
- III) adding at least one acid to the reaction mixture from step II) to

neutralize any remaining organic or inorganic base and to react with amine functionality in the product to solubilize the product;

IV) passing the resulting aqueous solution from step III) through an acid cation exchange column ( $H^+$  form); and

V) adding to the aqueous solution from step IV) a fluorometallic acid;

wherein the process is carried out in the absence of organic solvents, the aqueous solution obtained from the process is free from organic solvents, and wherein instead of step V) the at least one acid in step III) is a fluorometallic acid.

16. The process of claim 15 wherein in step II) the amine is N-methylethanolamine or N-methylglucamine.

17. The process of claim 15 wherein in step I) the phenolic polymer or copolymer is polyvinylphenol and the base is an alkali metal hydroxide; in step II) the aldehyde, ketone, or mixture thereof is anhydrous formaldehyde or paraformaldehyde; in step III) the at least one acid is phosphoric acid; and in step V) the fluorometallic acid is  $H_2 Ti F_6$  or  $H_2 Zr F_6$ .

18. The process of claim 17 wherein in step IV) the acid cation exchange column is a strong acid cation exchange column.

19. The process of claim 17 wherein in step I) the base is sodium hydroxide.

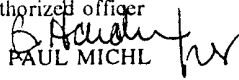
20. The process of claim 15 wherein after step V) the solution is again passed through an acid cation exchange column.

21. The aqueous solution prepared by the process of claim 1.

22. The aqueous solution prepared by the process of claim 15.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/19889

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :C08L 61/06 US CL :524/596 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 524/596 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,578,438 A (DEMMER et al) 25 May 1986, col. 17, lines 55-66.	21,22
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
*A*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E*	earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O*	document referring to an oral disclosure, use, exhibition or other means	*&* document member of the same patent family
*P*	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 25 NOVEMBER 1998		Date of mailing of the international search report <b>31 DEC 1998</b>
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No (703) 305-3230		Authorized officer  PAUL MICHL Telephone No. 703-308-2351