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The present invention relates to a process for separating higher molecular weight constituents from phenol polymers, in particular to the separation of higher-molecular compounds from optionally substituted phenol/ formaldehyde condensation products.

Phenol polymers are very important raw materials for the production of moulded articles and moulding compounds, protective coatings for metals or insulating materials in combination with epoxy resins. In the recent past, they have gained importance in new fields of application, for example, as fire-resistant fibers, as support materials for ion exchangers or as binders in copying materials, such as photoresists. For these new applications the polymers must, however, meet higher requirements. Commercially available phenol polymers contain certain amounts of low-molecular constituents, which for a number of uses bring about disadvantageous effects. Thus, the processing of phenol polymers at elevated temperatures causes serious environmental problems due to the high vapor pressure of the low molecular weight constituents, so that expensive exhaust appliances must be installed. Furthermore, the relatively high content of low molecular weight compounds is responsible for the low softening temperature of phenol polymers. This serious disadvantage in particular affects the application of phenol polymers at elevated temperatures, for example, their use as photoresist binders. At temperatures above about 140 °C the photochemically produced structures start to flow undesirably, which leads to an insufficient, poor resolution.

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From EP-A 0 144 880 it is known to perform a fractionated precipitation of novolaks in order to separate off undesired, low molecular weight constituents. For this purpose, the novolaks are dissolved in a suitable solvent and reprecipitated by adding a precipitant. This process necessitates a careful selection of the appropriate solvents or precipitants and a strict observance of the correct temperature, in order to be able to achieve reproducible results.

In DE-A 32 22 485 (equivalent to US-A 4,348,471), acid-free resins are described. Novolaks are treated with bases, for example, tertiary amines, in order to remove, by neutralization, the acid added for the preparation of the novolaks. No fractionating of the novolaks is described.

It was therefore the object of this invention to provide a process for separating higher molecular weight constituents from phenol polymers, in order to obtain a material having good heat resistance, a high molecular weight and a narrow molecular weight distribution range.

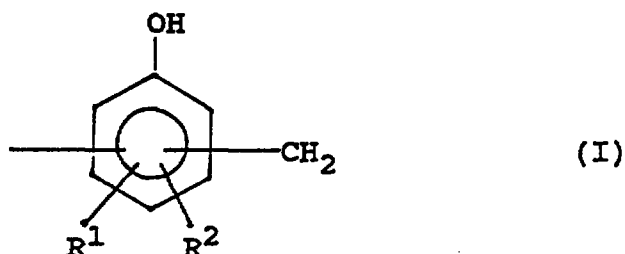
This object is achieved employing the initially described process, wherein the phenol polymer is dissolved in an organic solvent medium, the solution obtained is mixed, at room temperature, with ammonia or an amine, such that there is a stoichiometric deficiency of ammonia and amine, the precipitate is separated, dried, if appropriate, and treated with aqueous acid, and the resulting sediment is filtered off, washed and dried. The organic solvent medium used is an organic solvent or an organic solvent mixture. The solution is preferably mixed with 1 to 40 mole percent of ammonia or amine. The precipitate is preferably taken

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up in an organic solvent medium, which step is followed by a treatment with an aqueous acid.

The invention is illustrated by reference to the attached diagrams obtained from gel permeation chromatography (GPC diagrams). Figure 1 represents a GPC diagram of an untreated phenol polymer (recorded by means of a commercially available gel permeation chromatograph), with the molecular weight (M) being plotted against the calculation index (n) which is analogous to the quantity indicating the frequency of the individual molecules. Figure 2 represents the GPC diagram of the same phenol polymer, which has, however, been subjected to the treatment according to this invention. It is clearly visible that the peaks in the low molecular weight range have disappeared. The maximum of the curve shown in Figure 2 is shifted in the direction of increased molecular weights. At the same time, the range of molecular weight distribution is fairly narrower.

The term "phenol polymer" denotes polymers having phenolic hydroxy groups. In particular, a condensation product of optionally substituted phenol and formaldehyde is employed, which corresponds to the general formula I



in which

R_1 and R_2

are identical or different and denote hydrogen and/or branched or unbranched alkyl groups having one to nine carbon atoms.

Preferably,

R_1 denotes a hydrogen atom and

R_2 denotes a branched or unbranched alkyl chain having one to four carbon atoms, in particular a methyl group or tertiary butyl group.

Examples of preferably employed phenol polymers include novolaks of phenol, cresol or tert. butylphenol and formaldehyde. A survey of these compounds is given in "Chemistry and Application of Phenolic Resins", by A. Knop and W. Scheib, Springer Verlag 1979.

The phenol polymers which are suitable for the purposes of this invention are constituted by recurring units of identical or different structural composition.

The process according to this invention can generally be employed for the separation of high molecular weight constituents from polymers possessing phenolic hydroxy groups.

The molecular weight of the phenol polymers which can be used as starting materials for the process of this invention is not restricted by an upper limit. The lower limit is determined by the structure of the respective polymer and by its content of low molecular weight compounds. Preference is given to polymers having a molecular weight of more than 500.

The proportion of higher molecular weight constituents which can be separated off by means of the process according to the invention in general varies between 99.5 and 50 percent by weight, preferably between 99 and 60 percent by

weight, relative to the weight of the starting phenol polymer.

In the process of the invention, the organic solvent medium for the phenol polymers suitably comprises organic solvents, such as acetone, methyl-ethyl ketone, methyl-isobutyl ketone, the methyl, ethyl, propyl and butyl esters of acetic acid, methoxy-propyl acetate, methyl-glycol and alcohols, for example, ethanol, isopropanol and butanol or mixtures of these compounds. The selection of the appropriate solvents depends on the structure and polarity of the respective phenol polymers. If appropriate, the solvent medium can also contain unpolar organic solvents, for example, hydrocarbons, such as n-hexane.

In the process according to the present invention, an organic solution of the phenol polymer is treated with ammonia or an amine, such that there is a stoichiometric deficiency of ammonia or amine, respectively. It is supposed that this treatment causes an interaction between the acidic phenolic groups and the basic nitrogen, although other explanations are not excluded. Depending on the molecular size, this interaction results in a precipitation of the higher molecular weight constituents, whereas the lower molecular weight constituents remain in solution, and thus a separation takes place.

The addition is preferably effected dropwise and is continued as long as a precipitation is caused.

The amines, which can be used in the process of this invention apart from ammonia, are compounds which have an acid constant pK_a of more than about 6, measured in an

aqueous solution at about 25 °C. Preference is given to compounds whose pK_a exceeds about 9 (according to "Handbook of Chemistry and Physics", pp. D147 to D149, 58th edition, 1977).

Suitable amines include, for example, mono-, di- or tri-alkyl amines, such as ethyl amine, propyl amine, butyl amine, dimethyl amine, diethyl amine, dipropyl amine, dibutyl amine, trimethyl amine, triethyl amine, tributyl amine, ethylene diamine, cyclohexyl amine or piperidine.

Particular preference is given to triethyl amine, cyclohexyl amine, piperidine or ethylene diamine. It is also possible to use mixtures of the above amines.

The concentration of the initial organic solution of the phenol polymer in general ranges between about 1 and 50 percent by weight, preferably between about 5 and 40 percent by weight, relative to the weight of the solution.

The amount of ammonia or amine used in the process according to this invention preferably varies between about 1 and 40 mole percent, relative to the initially introduced phenol polymer.

In the process according to this invention, the phenol polymer, after having been dissolved in the organic solvent, is, as a rule, directly treated, at room temperature, with the amine or ammonia which is optionally dissolved in the solvent employed for the phenol polymer. The precipitate is separated off by means of a centrifuge or filter system and mixed with an aqueous acid solution, optionally after an intermediate drying step. Subsequently,

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the sediment, which is now free from low-molecular weight constituents, is dried using conventional methods.

The treatment of the organic solution of the phenol polymer with ammonia or the amine is performed at room temperature for a duration of 0.5 to 5 hours, but usually one hour will be sufficient to achieve satisfactory separation.

Treatment of the precipitate with aqueous acid can be effected by direct treatment of the dried substance. It is, however, preferred first to take up the precipitate in an organic solvent medium and then to treat it with aqueous acid.

Examples of suitable acids are inorganic or organic acids, such as hydrochloric acid, nitric acid, sulphuric acid, acetic acid, a.s.o., in their aqueous forms. The added amount of the acidic compound depends on the amount of ammonia or amine, which has been added before. In general, a slight excess of acid is employed, related to the added amount of ammonia or amine. Acidic ion exchangers can also be used successfully for liberating the phenol.

The process according to the present invention allows for an easy, uncomplicated separation of higher molecular weight phenol polymers from low molecular weight constituents. The polymers obtained in this way are color- and odorless powders which, compared to the starting materials, have increased molecular weights and narrower molecular weight distribution ranges. The substantial improvements achieved by this invention in respect of the thermal and mechanical properties of this kind of polymers, such as

glass transition temperature, film formation, tear strength, and the like, are obvious. Additionally, a liberation of monomers or other low molecular weight constituents upon heating of the polymers treated in accordance with this invention, is completely prevented. Thus, no problems occur due to impurities or sanitary hazards.

The present invention furthermore relates to fractions comprising the higher molecular weight constituents of phenol polymers, which have been obtained employing the process of this invention, and which possess a higher osmometric molecular weight and a higher glass transition temperature than the starting phenol polymer. Special preference is given to fractions whose osmometric molecular weight is increased by a factor of about 3 and whose glass transition temperature is increased by a factor of about 1.5.

From the phenol polymers according to this invention, moulding compounds are prepared employing known methods. Suitable fillers include inorganic mineral materials, such as limestone or glass fibers, or organic materials, such as woodflour. Due to the fact that the phenol polymers employed are virtually colorless, the moulding compounds prepared in this way can be dyed with a much wider range of colors than the materials known so far.

The increased glass transition temperatures of the phenol polymers employed result in an improved heat stability of the products made from these polymers.

The invention will be described in greater detail by the following, non-limiting examples.

Example 1

75 g of a novolak resin prepared by acid condensation of a mixture of m-, p- or o-cresol with formaldehyde are dissolved in 300 ml of ethyl acetate. 150 ml of n-hexane are added to this solution. After the insoluble constituents have been filtered off, 11 ml of triethyl amine are stirred in dropwise within 15 minutes. The colorless sediment which forms is removed by suction, washed with 200 ml of the solvent mixture and then dried in vacuo for 10 hours at room temperature.

23 g of the novolak treated in this way are dissolved in 250 ml of acetone and then dropwise stirred into 2.5 l of aqueous HCl having a strength of about 5 %. The precipitated polymer is sucked off, washed with distilled water until neutral and dried in vacuo for 24 hours at room temperature.

Analysis values of the untreated novolak and of the novolak treated in accordance with this invention:

	untreated	treated with amine/acid
osmometric molec. weight	1,180	3,690
glass transition temperature °C	88	126
M_n (from GPC)	1,400	3,300
M_w (from GPC)	13,300	18,050
non-uniformity (from GPC)	9.5	5.5

M_n denotes the number average molecular weight, and M_w denotes the weight average molecular weight. The non-uniformity is defined as the quotient $M_w:M_n$.

Example 2

150 g of a commercially available novolak (Alnovol® PN 430) are dissolved in 700 ml of isopropanol. Gaseous ammonia is blown into the solution with continuous stirring at room temperature, until no further precipitation is observed. The mixture is stirred for another 10 minutes, then the precipitate is filtered off and washed with 150 ml of isopropanol.

100 ml of the novolak treated in this way are dissolved in 200 ml of acetone and precipitated, with stirring, from 5 l of 1N H₂SO₄. The resulting novolak is washed with distilled water and then dried in vacuo for 24 hours at a temperature of 30 °C.

Analysis values of the untreated novolak and of the novolak treated according to the process of this invention:

	untreated	treated with amine/acid
osmometric molec. weight	800	2,400
glass transition temperature (°C)	89	121
M _n (from GPC)	1,400	4,000
M _w (from GPC)	6,900	20,800
non-uniformity	4.9	5.2

Example 3

50 g of a commercially available novolak (Alnovol® PN 320) are dissolved in 300 ml of ethyl acetate and 200 ml of n-hexane. Thereupon, 6 ml of triethyl amine are stirred in dropwise at room temperature. When the addition is completed, stirring is continued for another 10 minutes, then the precipitate is filtered off and washed with 150 ml of the solvent composition.

30 g of the novolak treated in this way are dissolved in 100 ml of acetone and precipitated, with stirring, from 3 l of 1N strength HCl. The novolak sediment remaining after washing with distilled water is dried in vacuo for 24 hours at 30 °C.

Analysis values of the untreated novolak and of the novolak treated by the process according to this invention:

	untreated	treated with amine/acid
osmometric molec. weight	655	2,360
glass transition temperature (°C)	71	90
M _n (from GPC)	1,060	2,800
M _w (from GPC)	3,640	7,275
non-uniformity	3.4	2.6

Example 4

125 g of a novolak resin prepared by acid condensation of a mixture of m- and p-cresol with formaldehyde are dissolved in 400 ml of a mixture of ethyl acetate and hexane (2:1 parts by volume). 22 ml of piperidine are then added dropwise while the solution is vigorously stirred. The precipitate is removed by suction and washed with solvent composition.

To check whether complete precipitation has been achieved, another 12 ml of piperidine are added to the filtrate. No precipitation occurs. 40 g of the isolated sediment are dissolved in 100 ml of acetone and dropwise added, with stirring, to 3 l of 1N strength H_2SO_4 . The sediment is removed by suction, washed and dried in vacuo. (Yield : 28 g)

Analysis values of the untreated novolak and of the novolak treated according to the process of this invention:

	untreated	treated with amine/acid
osmometric molec. weight	1,070	3,350
glass transition temperature ($^{\circ}C$)	87	128
M_n (from GPC)	1,350	3,800
M_w (from GPC)	11,600	16,200
non-uniformity	8.6	4.3

Application Example 1

Production of a moulding compound from a high molecular weight novolak and hexamethylene tetramine:

35 p.b.w. (parts by weight) of a high molecular weight novolak, prepared according to the process of this invention as described in Example 2 from a commercially available phenol resin (Alnovol® PN 430), are well mixed with 5 p.b.w. of hexamethylene tetramine, 50 p.b.w. of woodflour, 15 p.b.w. of limestone, 1 p.b.w. of zinc stearate and 1 p.b.w. of magnesium oxide. Further intimate mingling of the individual constituents is achieved by a calendering treatment performed at 100 °C. Then the composition precondensed due to the calendering treatment is finely ground and moulded at a temperature of 160 °C and a pressure of 100 kg/cm². The heating time is about 1 minute per 1 mm of layer thickness.

Utilitarian tests of the moulded articles produced in this way give the following results:

Bending strength: 80 N/mm²

Temperature of deflection 140 °C
under load (Martens):

These values demonstrate the advantages of the novel novolaks: due to their increased glass transition temperature, the temperature of deflection under load is considerably higher than the values which can conventionally be achieved with compositions of this kind, i.e., about 70 N/mm² and about 125 °C.

Application Example 2

Preparation of a photoresist using a high molecular weight novolak possessing an increased heat stability:

7 p.b.w. of a high molecular weight novolak prepared from a cresol/formaldehyde condensate by means of the process of this invention, and
3 p.b.w. of the esterification product obtained from 1 mole of 2,3,4-trihydroxybenzophenone and 3 moles of naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid chloride,
are dissolved in
45 p.b.w. of methyl-ethyl ketone and
45 p.b.w. of ethanol.

The solution obtained is filtered through a filter having a pore diameter of 0.2 μm and spin-coated onto a superficially oxidized silicon wafer and dried. The resulting layer thickness is about 1.7 μm .

The wafer is subjected to contact exposure through a test mask, exposure being performed for 15 seconds with an intensity of 4.5 mJ/cm^2 , at 365 nm, and is developed with a solution containing 5.3 p.b.w. of sodium metasilicate, 3.4 p.b.w. of trisodium phosphate and 91.3 p.b.w. of water.

The resulting image pattern has a resolution of about 1.0 μm .

Then the structured resist layer is baked for 30 minutes at 150 °C. A microscopic examination of the resist structures does not reveal any rounding-off of the edges nor flowing of the resist lines.

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In contrast thereto, layers which contain the customary, untreated novolak binders no longer exhibit clear structures after being heated in the way described above. The structures show rounded-off edges and are much wider than they were initially. In some places, there is even observed a formation of webs between the individual lines.



CLAIMS

1. Process for separating higher molecular weight constituents from phenol polymers, characterized in that the phenol polymer is dissolved in an organic solvent medium, the solution obtained is mixed, at room temperature, with ammonia or an amine, such that there is a stoichiometric deficiency of ammonia or amine, the precipitate is separated, dried, if appropriate, and treated with aqueous acid, and the resulting sediment is filtered off, washed and dried.
2. Process as claimed in claim 1, characterized in that the organic solvent medium is an organic solvent or a solvent mixture.
3. Process as claimed in claim 1, characterized in that the solution is mixed with about 1 to 40 mole percent of ammonia or amine, relative to the phenol polymer.
4. Process as claimed in claim 1, characterized in that the dried precipitate is taken up in an organic solvent medium and then treated with aqueous acid.
5. Process as claimed in claim 1, characterized in that the phenol polymer is a condensation product of, optionally substituted, phenol and formaldehyde.
6. Process as claimed in claim 1 or 3, characterized in that the amine is a compound which in an aqueous solution of 25 °C has an acid constant pK_a of more than about 6.
7. Process as claimed in claim 1 or 6, characterized in that the amine is triethylamine.
8. Process as claimed in claim 1 or 6, characterized in that the amine is piperidine.