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(72) Inventeurs/Inventors:
CHUM, HELENA L., US;
KREIBICH, ROLAND E., US

(73) Propriétaire/Owner:
MRI VENTURES, INC., US

(74) Agent: RIDOUT & MAYBEE LLP

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(54) Title: NOVOLAK RESIN FROM FRACTIONATED FAST-PYROLYSIS OILS

(57) Abrégé/Abstract:
A process for preparing phenol-formaldehyde novolak resins and molding compositions in which portions of the phenol normally contained in said resins are replaced by a phenol/neutral fractions extract obtained from fractionating fast-pyrolysis oils.

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(71) Applicant: MRI VENTURES, INC. [US/US]; 425 Volker Boulevard, Kansas City, MO 64110 (US).

(72) Inventors: CHUM, Helena, L. ; 8448 Allison Court, Arvada, CO 80005 (US). KREIBICH, Roland, E. ; 4201 South 344th Street, Auburn, WA 98001 (US).

(74) Agent: NORRIS, Jerome, J.; Browdy and Neimark, 419 Seventh Street, N.W., Suite 300, Washington, DC 20004 (US).

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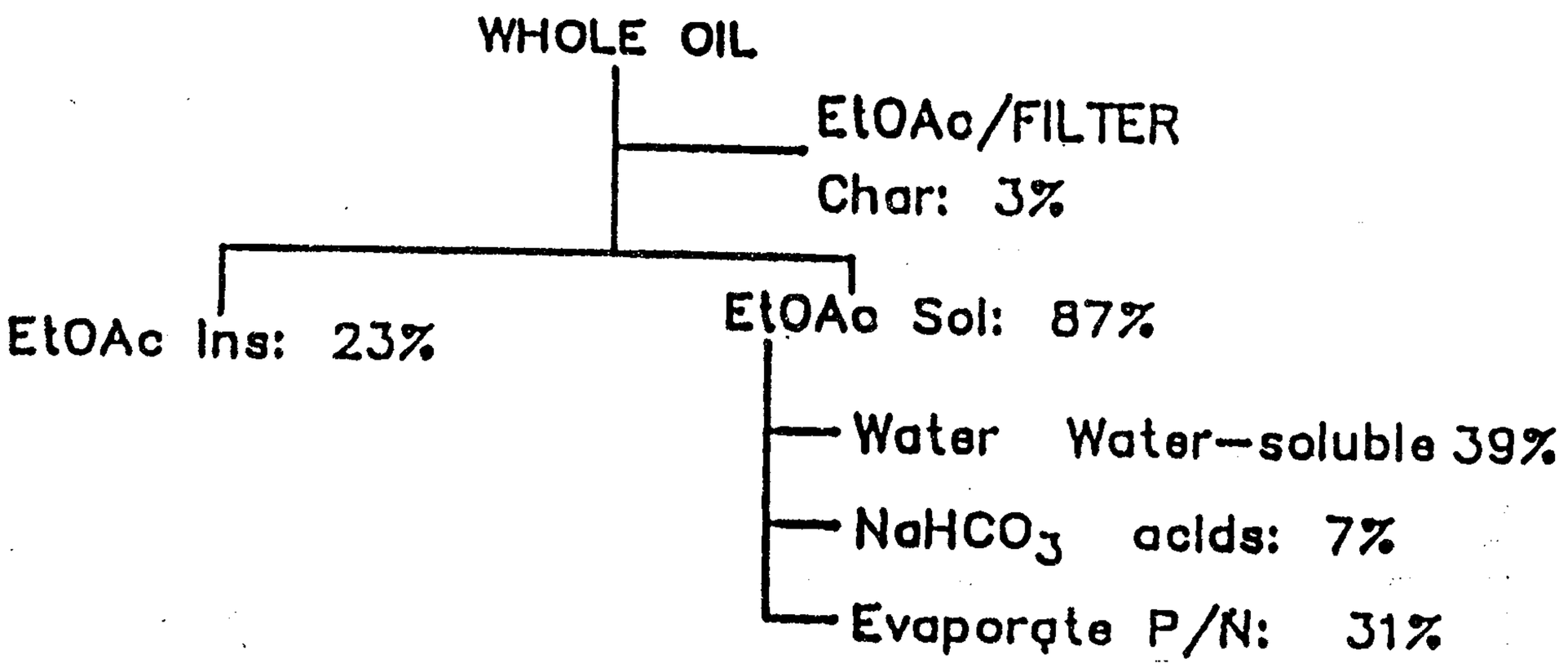

(57) Abstract

A process for preparing phenol-formaldehyde novolak resins and molding compositions in which portions of the phenol normally contained in said resins are replaced by a phenol/neutral fractions extract obtained from fractionating fast-pyrolysis oils.

"NOVOLAK RESIN FROM FRACTIONATED FAST-PYROLYSIS OILS"

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention under Contract No. DE-AC02-83CH10093 between the United States Department of Energy and the Solar Energy Research Institute, a Division of the Midwest Research Institute.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The invention relates to the production of novolak resins from biomass materials and, more particularly, to the treatment of fast-pyrolysis oils derived from lignocellulosic materials to make novolak resins. Specifically, the present invention relates to taking phenol/neutral fractions and rendering them suitable for the production of novolak resins, subsequent to obtaining said fractions from fast-pyrolysis oils derived from lignocellulosic materials.

2. DESCRIPTION OF THE PRIOR ART

Adhesive resins such as resoles are utilized in a wide variety of applications, inclusive of which is the bonding of wood layers to manufacture plywood, and adhesive resins such as novolaks are used in the formation of molded pieces and articles, and the like. However, certain disadvantages are attendant to existing techniques for manufacturing these different types of phenolic resins.

For example, phenol has been traditionally derived from petroleum-based products; however, the production of petroleum-based phenol is quite expensive, and efforts in the industry in recent years have been to at least partially substitute the phenol in such resins with inexpensive phenols derived from wood-based products or extracts. More specifically, phenols derived from bark, wood chips and the like have been looked at as a potential substitute for petroleum-based phenol in such resins.

The pyrolysis of biomass, and in particular lignocellulosic materials, is known to produce a complex mixture of phenolic compounds. In nature, lignin acts as an adhesive to bind the cellulose fibers together. Therefore, lignin and lignin-derived material from wood would appear to be a natural starting point for the development of biomass-based adhesive resins. Sources for such phenolic materials include black liquor from kraft pulping and other pulping processes, where the lignin is present in a stream which is commonly burned to recover process heat and chemicals.

Unfortunately, these lignins are generally not very reactive after recovery for a variety of reasons, such as high molecular weight, chemical modification during recovery due to condensation reactions and the like, and lack of reproducibility of properties. Various types of pyrolysis processes have also been utilized, frequently yielding similar kinds of results; however, fast-pyrolysis, which proceeds at temperatures between about 450°C to about 600°C and has short vapor residence times in the order of seconds has not been used.

Fast-pyrolysis of biomass features the depolymerization of cellulosic, lignin, and hemicellulosic polymers which produces an oil having a relatively low molecular weight and which has considerable chemical activity under proper conditions. Crude pyrolysis oil apparently undergoes a limited amount of repolymerization

due to condensation. However, the thermal stability of fast-pyrolysis oils at room temperature is qualitatively quite good imparting a good shelf life for the oils, although at 100°C the crude oils solidify overnight. Solidified pyrolysis oils are characterized by their low strength and brittleness. The potential of pyrolysis products for use in adhesive resins is not a new concept, as indicated above, but the efficient and cost-effective reduction of this to practice has been an elusive goal over many years.

The general approach of producing phenols from biomass has previously been to purify the phenolic fractions present in the pyrolysis oils by the use of solvents to partition the constituents by differences in solubility and reactivity. Different variations of solvents, reagents, and sequence of extractions have been developed in the past, and this has resulted in different partitioning coefficients for a couple of hundreds of chemical compounds known to be in pyrolysis oils, and therefore produced extracts having differing relative compositions. Another significant difference between various research efforts pertaining to this area in the past has been the type of pyrolysis process used to produce the oils used as feed in the extraction process. These include updraft gasification, entrained fast-pyrolysis, and fluidized bed fast-pyrolysis, all at atmospheric pressures, as well as slow, high pressure liquefaction processes. In addition, both hardwoods and softwoods have been used as feedstock in the past for the oil forming processes. These differences in extraction and pyrolysis processes, coupled with the differences in feedstock, yield different materials as products. Thus, the usefulness of a particular extract as an adhesive component is quite different, one from the other.

U.S. Patents No. 4,209,647 and 4,223,465 disclose methods for recovering phenolic fractions from oil obtained from pyrolysis of lignocellulosic materials

and the subsequent use of that fraction in making of phenol-formaldehyde resins. However, these processes use pyrolysis oils which are usually formed at ill-defined temperatures and which have undergone phase separation cracking and some condensation, and suffer from very low yields.

A number of other patents including U.S. Patents No. 2,172,415, No. 2,203,217, No. 3,069,354, No. 3,309,356 and No. 4,508,886 as well as Japanese Patent No. 38-16895 all disclose a variety of processes for recovering phenolic fractions from oils derived from biomass materials and soil resources. These processes vary in the particular procedures and techniques utilized to ultimately separate the phenolic fractions as well as the procedures utilized to derive the oil from the biomass or other feed material. However, they all have a common thread linking them in that the ultimate end product is a phenolic fraction, which is desired to be as pure as possible. This phenolic fraction is then utilized to produce phenol-formaldehyde resins. The phenol substitutes usually were slower than phenol derived from petroleum-based products. The complex procedures disclosed in these references to produce relatively pure phenolic fractions are not particularly economical. Thus, there is still a need for a process designed to produce pyrolysis oils from lignocellulosic materials and then extract a phenolic composition from such oils which is capable of functioning as efficiently as petroleum-based phenols in the formation of phenol-formaldehyde resins and which is less expensive to produce.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide two stage phenolic resins or novolaks, in which the phenol content is in part replaced by a phenol/neutral fractions (P/N) from fast pyrolysis oils derived from lignocellulosic materials.

Another object of the present invention is to provide inexpensive molding compositions comprising two stage phenolic resins or novolaks, in which the phenol content is in part replaced by a phenol/neutral fractions (P/N) from fast-pyrolysis oils derived from lignocellulosic materials.

To achieve the foregoing and other objects and in accordance with the purpose of the present invention, as embodied and broadly described herein, a process is disclosed for fractionating fast-pyrolysis oils to produce phenol-containing compositions suitable for manufacturing phenol-formaldehyde resins. The process includes admixing the oils obtained from the fast-pyrolysis process with an organic solvent having a solubility parameter of about 8.4-9.1 $[cal/cm^3]^{1/2}$ polar components in the 1.8-3.0 range and hydrogen bonding components in about the 2 to 4.8 range to extract the phenol and neutral fractions from the oils. The organic solvent-soluble fraction containing the phenol and neutral fractions is separated from the mixture and admixed with water to extract water-soluble materials therefrom. The organic solvent-soluble fraction is then separated from the water fraction and admixed with an aqueous alkali metals bicarbonate solution to extract strong organic acids and highly polar compounds from the solvent fraction. The residual organic solvent-soluble fraction is separated, and the organic solvent is removed therefrom to produce the phenol/neutral fractions (P/N).

In general, preparation of novolaks is accomplished by heating the P/N fractions and phenol with an acid catalyst and slowly adding formaldehyde with heating under constant stirring. After formaldehyde addition, the batch can be kept at 98-100°C for some time and a sodium carbonate solution can be slowly added to neutralize the acid catalyst. The resin is then washed with hot water and dried in an oven with circulating air.

In preparing a molding composition from the novolak prepared according to the invention, the novolak

resin is rolled into sheets, ground and mixed with hexamethylene tetramine and lime and cured at high temperatures and pressures to produce molding materials having comparable tensile, flexure and Izod impact values as novolak molding materials without the P/N fraction.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings which are incorporated in and form a part of the specification illustrate preferred embodiments of the present invention, and together with the description, serve to explain the principals of the invention. In the drawings:

Fig. 1 is a flow diagram illustrating the process of fractionating the fast pyrolysis oils to produce the P/N fractions used in the present invention;

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

During the course of studying the problem of producing inexpensive but effective phenolic compositions from biomass, it was discovered that certain polar organic solvents having at least a moderate solubility parameter, moderate degree of polarity, and good hydrogen bonding capabilities were capable of extracting both phenol and neutral fractions from fast-pyrolysis oils. Moreover, it was discovered that this extraction technique was equally effective for fast-pyrolysis oils of differing starting materials. Thus, it was discovered that the present invention may be utilized with pyrolysis oils derived form redwood, pine sawdust, bark, grasses, softwoods as well as certain hardwoods with very little differences in the final results. Apparently, the fast-pyrolysis process preserves the delicate products in monomeric and oligomeric states. A key factor in the process of the present invention is that the oils derived from the lignocellulosic materials must be done so utilizing a fast-pyrolysis. Fast-pyrolysis is generally known in the art, and such a technique has been specifically disclosed

in an article entitled, "Production of Primary Pyrolysis Oils in a Vortex Reaction", American Chemical Society Division of Fuel Chemistry Preprints, Vol. 32, No. 2, pp. 21-28 (1987). Thus, details of such fast-pyrolysis techniques need not be specifically repeated and disclosed herein, and the contents of this Article are therefore specifically incorporated herein by reference. Oils from other fast-pyrolysis concepts are also good feedstocks. Such concepts are referenced in "Fast-Pyrolysis of Pretreated Wood and Cellulose", Ibidem, pp. 29-35 (1987), and "Preliminary Data for Scale up of a Biomass Vacuum Pyrolysis Reactor", Ibidem, pp. 12-20 (1987); "The Role of Temperature in the Fast-Pyrolysis of Cellulose and Wood", Industrial Engineering Chemistry Research", Vol. 27, pp. 8-15 (1988), and "Oil From Biomass by Entrained flow Pyrolysis", Biotechnology and Bioengineering Symposium, No. 14, pp. 15-20 (1984).

The preferred biomass solids in such fast-pyrolysis of biomass solids entrain the feedstock particulates tangentially at high velocities into a vortex reactor tube which has an internal surface design that guides the centrifuged solids into a tight helical pathway on the reactor wall. This results in a very high heat transfer to the wood or other feedstock particles which allows mild cleavage of the polymeric components of the feedstock. Consequently, high yields (greater than 55%) of dry woods and bark oils are generally obtained. If the feedstock is not fully pyrolyzed, the solids enter a recycle loop located at the end of the vortex reactor. After attrition to a powder, char particles elute with the vapor stream and are isolated in a char cyclone. Alternative methods to the preferred fast pyrolysis process described produce primary pyrolysis oils useful as starting materials for the process of this invention and include fast-pyrolysis in fluidized beds and in entrained flow reactors.

Utilizing the process of the present invention, the pyrolysis oils are fractionated in a unique way which produces a combined phenolics and neutral fraction of high phenolic hydroxyl and aldehyde content. In general, a polar organic solvent is added to the oils to separate the phenol and neutral fractions from said oils. The organic solvent-soluble fraction is then admixed with water to extract water-soluble materials, and then further washed with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds. The residual organic solvent-soluble fraction containing the phenol and neutral fractions is then isolated, and the organic solvent is removed, preferably by evaporation, to produce a phenol-containing composition having the phenol and neutral fractions of the original raw oils. The yield of the phenolics and neutrals fraction in the extract is about 30% of the fast-pyrolysis oil derived from sawdust and about 50% of the oil derived from bark.

In prior art phenol-producing processes, the processes ended only after the phenolic-containing compositions were generally reduced to purified phenolics only, with the neutral fractions also being removed. By neutral fractions, it is meant those compounds which are not solubilized by a strong base such as sodium hydroxide, and have molecular weights of approximately 100-800. Such neutral fractions include carbonyl compounds, furfural-type compounds and the like. It was apparently previously believed that such neutral fractions must also be extracted in order to provide a phenol composition which may be utilized as a substitute for petroleum based phenols in the production of phenol-formaldehyde adhesive resins. It has been discovered, however, that by utilizing the process of the present invention, the resultant composition containing both phenol and neutral fractions function just as well as and in some aspects better than a relatively pure phenol composition in the production of phenol-formaldehyde resins because, since

the compositions have aldehyde groups, much less formaldehyde is needed to make these formulations. Reduced formaldehyde levels lead to minimization of potential environmental problems. In addition, the economics are such that, it is substantially less expensive to manufacture the combined phenol and neutral fraction composition. Moreover, by utilizing the entire fraction which includes phenolic compounds and neutral compounds as feedstocks for resins, it was found that this prevented the pyrolysis-derived reactive phenolics from undergoing air oxidation under alkaline conditions, which is what prevails when one isolates and purifies the phenolics fraction alone. This latter air oxidation which can be a problem is a type of condition that prevails in many prior art techniques and is accomplished by extractions with aqueous sodium hydroxide solutions, and accompanied by the formation of insoluble tars and reduced yields of phenolics.

Investigations of the fractionation scheme of the present invention as generally described above utilizing pine fast-pyrolysis oils were carried out employing a number of different solvents to determine the preferred and optimum solvents and the requirements thereof. In general, the whole oil was first dissolved in the organic solvent preferably in an oil:solvent ration of 0.5:1 to 1:3 by weight. The oil was initially filtered to separate char which is carried over from the pyrolysis reactor operations. Upon standing, the solvent/oil mixture then separates into two phases, the solvent-soluble phase and the solvent-insoluble phase.

One requirement for the organic solvent is that the solvent and water exhibit low mutual solubility. Preferably, acceptable solvents include those with solubilities that are not more than about 10 grams of solvent in 100 grams of water and about 3 grams of water in 100 grams solvent, in terms of mutual solubility.

Thus, this solvent requirement eliminates all low-molecular-weight alcohols (methanol, ethanol, propanol) that are infinitely soluble in water, methylethylketone, the carboxylic acids (formic, acetic and propionic) which are infinitely soluble in water, and methyl formate. The classes of solvents that would be acceptable only from a pure mutual solubility point of view include hydrocarbons (aliphatic, aromatic), higher alcohols (greater than 6 carbon atoms), higher ketones (greater than 5 carbon atoms), esters (greater than 2 carbon atoms), ethers, polychlorinated hydrocarbons, and higher nitriles (greater than 4 carbon atoms).

Another requirement for the organic solvent which further limits potential candidates is that the solvent must have a low boiling point or a low-boiling point azeotrope. The preferred boiling point is around 100°C, although this is somewhat relative. Yet another requirement for the organic solvent is that the solvent have some degree of polarity, preferably high polarity, as well as high hydrogen bonding capability in addition to a moderate-to-good solubility parameter. The solubility parameter is defined as a measure of all the intermolecular forces present in the solvent and is determined by the three-component Hansen parameters commencing on page 141 of the "CRC Handbook of Solubility Parameters and Other Cohesion Parameters" by Allan F.M. Barton, 1983. The overall solubility parameter is composed of components due to dispersive forces, polar forces (caused by a high dipole moment in the molecule), and hydrogen bonding capability. Solubility parameters, measured in $[cal/cm^3]^{1/2}$, range from 5-7 for hydrocarbons and non-polar solvents, to 14.5 for methanol and 23.4 for water-highly polar substances. Thus, low boiling point ethers, such as diethyl ether, are excluded from being preferred solvents since they have a very low solubility parameters (7.4) and very low polar components (1.4). Hydrocarbons are also excluded as preferred solvents

because of their very low polar components and overall low solubility parameters.

It has been found that the preferred group of solvents for use in the present invention include acetate and propionate esters, methyl alkyl ketones and ethyl alkyl ketones. More specific preferred organic solvents are listed below in Table I, the most preferred being ethyl acetate due to its availability, relatively low solubility in water, and high oil solubility. The most preferred range for solubility parameters includes 8.4-9.1 with polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.5 range. Additional acceptable solvents are the isomers of those listed in Table 1. Mixtures of esters are also acceptable as are mixtures of the higher ketones. Ternary solvent systems also are possible, primarily mixtures of esters and high molecular weight ethers such as diisopropylether to reduce the boiling point. However, the most preferred solvents for use with the present invention are ethyl acetate, as indicated above, as well as butyl acetate and methylisobutylketone.

TABLE I

	Acetate Esters			Methyl Ketones			Ethyl Ketone
Property	Ethyl	Propyl	Butyl	i-Butyl	i-Amyl	i-Propyl	Ethyl
Mol. Wt	88.1	102.1	116.2	100.2	114.2	86.14	86.14
Boiling Point, °C (at 70 mmHg)	77.1	101.5	126.1	116.5	144	92	102.0
Density, 20°C	0.90	0.89	0.88	0.80	0.88	0.81	0.81
Heat Vaporization, kcal/mole (20°C)	8.4	9.3	10.4	10.00			
kcal/mole (b.p.)	7.71	8.20	8.58	8.50		7.73	8.06
Solubility, wt% in water	8.08	2.3	0.43	1.7	~0	~2	2.4
Water in Azeotrope	2.94	3.9	1.86	1.9	~0	~2	2.6
Water wt%	9.47	14	28.7	24.3	44.0		24
boiling point, °C	70.38	82.2	90.2	87.9	94.7		82.9
Dielectric Constant	6.02	6.00	5.01	13.11			17.0
Solubility param. Total	9.1	8.4	8.46	8.57	8.55	8.5	8.8
Dispersive comp.	7.44	6.6	7.67	7.49	7.80		~7.8
Polar comp.	2.6	2.0	1.8	3.0	2.8		~3.4
H-Bonding comp.	4.5	4.8	3.1	2.0	2.0		2.0

As indicated above, the preferred solvent is ethyl acetate, and the process of the present invention will hereinafter be described in terms of utilizing ethyl acetate as the solvent. However, it should be understood that any of the identified solvents may be utilized in the following described process. As previously indicated the whole oil is dissolved in the ethyl acetate at a preferred pH of about 2-4 and then filtered. Upon standing, the ethyl acetate/pyrolysis oils mixture separates into two phases. Chemical spectroscopic analysis revealed that the ethyl acetate-insoluble fraction contains carbohydrate and carbohydrate-derived products. The ethyl acetate-soluble fraction, containing the phenol/neutral fractions, is then separated and washed with water to remove the remaining water-soluble carbohydrate and carbohydrate-derived materials, preferably in a 1:6 to 1:1, water:oil weight ratio. The ethyl acetate-soluble fraction is then further extracted with an aqueous metal bicarbonate solution, preferably a 5% by weight aqueous solution of sodium bicarbonate. The pH of the bicarbonate extraction solution is preferably maintained at approximately 8-9.5, and a 6:1 to 0.5:1 bicarbonate solution:oil weight ratio is preferably utilized. The aqueous bicarbonate layer extracts the strong organic acids and highly polar compounds, and the remaining ethyl acetate-soluble layer contains the phenols and neutral fractions. This ethyl acetate-soluble layer is then separated, and the ethyl acetate solvent is evaporated using any known evaporation technique, including vacuum evaporation techniques. The dried phenol/neutral fraction typically contains 0.5-1% of water with traces of ethyl acetate. Table II illustrates typical yields for various pine sawdust fast-pyrolysis oils and fractions of oils obtained during different test runs as well as for Douglas fir bark fast-pyrolysis oils.

TABLE II

Yields for Various Pyrolysis Oils

Pyrolysis Oil	Wt % Yields of Pyrolysis Oils Based on Dry, Char-Free Oil			
	EtOAc Insol	Water Sol.	Organic Acids	Phenol/Neut
Pine sawdust	42.8	24.7	5.7	21.3[a]
Pine sawdust	28.2	39[c]	6.1	26.7[b]
Combined pine oil[d]	22.8	28.9	6.7	25
Pine sawdust	41 [e]	27.2	6.3	26
Douglas fir bark	0	12.1	15 Solids: 2.9	Phenols: 47.8 Neutrals: 15.6
Douglas fir bark	0	ND*	19 Solids: 4.8	Phenols: 50.8 Neutrals: 17

[a] Phenolics: 16.5; Neutrals: 9.5
[b] Phenolics: 16.5; Neutrals: 6.0
[c] Water solubles by difference
[d] From two condensers
[e] EtOAc insolubles by difference
*Not Determined

As indicated in Table II, the aqueous alkali metal bicarbonate solution utilized to extract strong organic acids and highly polar compounds further purifies the phenol/neutral fractions. While any suitable alkali metal bicarbonate solution may be utilized, the preferred solution is selected from sodium bicarbonate, potassium bicarbonate, lithium bicarbonate and ammonium bicarbonate, with sodium bicarbonate being the preferred and most optimal solution. From the aqueous bicarbonate solution, it is possible to isolate a fraction rich in organic acids as a by-product. In this instance, the aqueous layer can be neutralized, for example with 50% by weight of phosphoric acid (although other acids can be used) saturated with sodium chloride, and extracted with ethyl acetate. It is possible to then evaporate the solvents and isolate the remaining fractions as well.

The phenols/neutrals fraction can be further fractionated into isolated phenolics and neutrals if desired. This can be accomplished by utilizing a 5% by weight solution of sodium hydroxide in a volume ration of 5:1 of solution:extract. The aqueous layer is then acidified to a pH of about 2 utilizing a 50% solution of phosphoric acid (although other acids can be used). It is then saturated with sodium chloride and extracted with ethyl acetate. evaporation of the solvent leads to the isolation of the phenolics fraction; evaporation of the initial ethyl acetate solution freed from phenolics leads to the neutrals fraction. It should be noted, however, that the present invention does not require this separation of the phenol from the neutral fractions, and it is in fact this aspect of the present invention which makes the present process so economical. In the past, as previously indicated, the phenolics have always been the desired end-produce, and sodium hydroxide has typically been utilized in such process treatment. This is unnecessary with the process of the present invention, since it has been discovered that the combined phenolic

and neutral fraction composition is sufficiently pure to function by itself in the formation of adhesive resins.

The process of the present invention can be operated in both batch mode as well as in a continuous mode. In the batch mode embodiment, the whole oils are extracted with ethyl acetate and then washed with water. Following the water wash, the composition is then washed with the aqueous sodium bicarbonate to eliminate the acidic components, which come from pyrolysis of the carbohydrate fraction and would be deleterious to the resins. In a continuous operation, the pyrolysis oils is preferably extracted simultaneously with water and ethyl acetate, and then the ethyl acetate's soluble fraction is extracted countercurrently with the aqueous bicarbonate solution. The whole ethyl acetate fraction, which includes both phenolic and neutrals compounds, is then utilized as a feedstock for resins after solvent evaporation.

EXAMPLE 1

1.0 kg of fast-pyrolysis oil derived from pine sawdust was dissolved into 1 kg of ethyl acetate. After filtration of the solution, this solution then separated into two easily identified and separated phases. The ethyl acetate-soluble phase was then isolated, and 0.8 kg of water was added to this phase. The resulting water-soluble fraction was isolated and saved for further processing. 2 kg of 5% sodium bicarbonate solution was then added to the ethyl acetate-soluble fraction, and the aqueous phase therefrom was saved for further processing. This aqueous phase was the acids-soluble fraction. The resulting washed ethyl acetate-soluble solution, containing the phenol and neutral fractions, was then solvent evaporated to remove the ethyl acetate solvent. The yield of phenol/neutral was 31% by weight based on the dry oil.

The remaining etnyl acetate-insoluble fraction was solvent evaporated and yielded weight percent of the starting dry oil. The aqueous wash yield after solvent evaporation was 39 weight percent of the oil. The aqueous bicarbonate solution was neutralized with a 50% phosphoric acid solution, and after saturation with sodium chloride, the organic phase was extracted into ethyl acetate. After solvent evaporation, the acids fraction yield was approximately 7 weight percent. Fig. 1 illustrates this mass balance of the various fractions resulting from this Example I utilizing the process of the invention.

EXAMPLE II

9.5 kg of fast-pyrolysis oils derived form pine sawdust were dissolved into 10 kg of ethyl acetate. After filtration, this solution settled into two easily identified and separated phases. 1.8 kg of water was then added to the ethyl acetate-soluble phase, and this solution was then separated into two easily identified and separated phases. The resulting water-soluble fraction was saved for further processing, and the other ethyl acetate-soluble fraction was then admixed with 8.9 kg of a 5% sodium bicarbonate solution. The aqueous phase of this solution was then separated and saved for further processing, which was the acids-soluble fraction. The resulting washed ethyl acetate-soluble solution, containing the phenol/neutral fraction was separated, and the solvent was then evaporated. The yield of the phenol/neutral fraction was 30% by weight based on dry oil.

Using a procedure similar to that described above in Example I, the mass balance of the fractionation was determined as follows: the ethyl acetate insoluble fraction comprises 21 weight percent, the water-soluble fraction comprises 31 weight percent, and the organic acids comprise 7.2 weight percent.

EXAMPLE III

The fractionation of Douglas fir pyrolysis products which are solids at room temperature, was similar to that described for pine. 4.6 kg of Douglas fir fast-pyrolysis product were dissolved into 9.8 kg of ethyl acetate solution. No ethyl acetate insoluble fraction was observed. The whole solution was then extracted with 12 kg of a 5 weight percent aqueous sodium bicarbonate solution. The ethyl acetate-soluble solution contained 68 weight percent of phenolics and neutrals. The phenols and neutrals were then separated by extraction with 11 kg of a 5 weight percent aqueous solution of sodium hydroxide. From the ethyl acetate solution, 17 weight percent of neutrals were obtained. The alkaline aqueous solution containing the phenolics was acidified with 50% phosphoric acid (although other acids could have been used). This solution was then saturated with sodium chloride and extracted with ethyl acetate to yield 50.8 weight percent for the phenolics fraction upon solvent evaporation. In the extraction with aqueous bicarbonate solution, a precipitate was formed (5 weight percent) along with the soluble acids fraction of 19 weight percent. The date for the fractionated materials are provided in Table II above.

EXAMPLE IV

Fast-pyrolysis oil derived from pine sawdust also fractionated on a continuous basis. This continuous process utilized, but is not limited to, a 6-stage system of mixer tanks and settling tanks. The oil, ethyl acetate and water were mixed and allowed to settle, with the organic phase being sent on to multi-stage extraction with 5 weight percent aqueous sodium bicarbonate solution with each extraction stage having a separate settler tank. The bicarbonate extraction was run countercurrent to the flow of the organic phase. The aqueous fractions, that is the combined ethyl acetate insoluble and water-soluble

fractions, the aqueous bicarbonate solution, and the organic phase were all collected and processed as described above. Conditions of the extraction included the following: oil flow, water flow, ethyl acetate flow, and aqueous bicarbonate flow rates were 10, 6, 34 and 35 mL/min, respectively. It should be noted, however, that the countercurrent continuous extraction process is not limited to these flow rates. The yield of phenol/neutral fraction composition was about 20% based on the oil flow rate and phenol/neutral isolated fractions. A total of 20 kg of oil was fractionated in this way. Variations in flow rates and number of settler and mixer tanks, however, can yield different proportions of materials. Phase separation was readily accomplished within the settlers.

Analysis of the products for intermediate stages of extraction revealed that 1-3 stages of bicarbonate extraction may be used. Turning from the Examples given above, the fractionation scheme described above allowed the isolation of 21% to 31% of the starting pine oils as a phenol/neutral fraction, or overall yields of 12-21% based on starting dry wood. This fraction consisted of approximately 73% phenolics, extractable from sodium hydroxide solution from an ethyl acetate solution, and 27% neutrals. The total yield of phenol/neutral fraction isolation is reproducible as shown by the runs in Table II above.

The typical oil contained 6.2% phenolic hydroxyl and 0.4% carboxylic acid contents by weight ranges. Ranges of 5.5-6.5% phenolic hydroxyl and 0.1-0.6% carboxylic acid contents are expected for the different starting feedstocks. The phenol/neutral fraction included about 6.6% phenolic hydroxyl content and no carboxylic acid content. Expected ranges for phenols/neutrals are 6.0-12% depending on the feed. The acids fraction included about 9.2% phenolics and 0.9% carboxylic acid contents. Ranges for various feedstocks are 5-10% for phenolics and 0.5-3% carboxylic acid contents.

In characterizing the resultant phenol compositions, the apparent molecular weight distributions obtained from gel permeation chromatography on polystyrene-divinylbenzene copolymer gels (50 Angstrom) with tetrahydrofuran as solvent, indicated that the phenolics fraction had components ranging from the monomeric substituted phenols (around 150) to oligomers (up to several thousand in molecular weight). The acids and neutrals had the lowest molecular weight components. From molecular beam mass spectra of the phenol/neutral fractions, a number of phenolic compounds were detected: guaiacol (2-methoxyphenol) m/z 124; catechols m/z 110; isomers of substituted 2-methoxyphenols with alkyl groups such as methyl (m/z 138), vinyl (m/z 150), 3-hydroxy-propen(1)-y1 (m/z 180), allyl (m/z 164), hydroxyethyl (m/z 168), and ethyl (m/z 152), most likely in the p-position. In addition, carbohydrate-derived compounds were present such as furfural alcohol and a number of other furfural derivatives.

From proton nuclear magnetic resonance spectrum of the phenol/neutral fraction, of the total intensity, the aromatic protons (6.5-10 ppm) constituted 52%, the aliphatic (1.5-3.5 ppm) about 20%, and the methoxy region and oxygenated and side-chain region (3.0-4.2 ppm) constituted 30%. This was in agreement with the description from the molecular beam mass spectra of mixtures of phenolics with substituted groups. The carbon-13 nuclear magnetic resonance spectra confirmed this data.

Bark derived phenols have a very high phenolic hydroxy content (7.4-11.5%) depending on pyrolysis conditions (steam to nitrogen carrier gas) and therefore are very suitable for adhesive formulation replacing phenol at greater than a 50% level.

As previously indicated, a principal purpose of producing the phenol/neutral fractions is to provide a substitute for pure phenol in the production of resins and

the like. Specifically, novolaks, which are phenol-formaldehyde resins formed under acid conditions, were produced and compared to novolaks utilizing standard formulations of commercially available phenol. Test novolak samples were then prepared and were characterized by solid-state carbon-13 cross polarization/magie angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra as well as solution NMR. The spectra of a phenol-formaldehyde novolak were compared with a similar novolak in which 50% by volume of the phenol was replaced with the phenol/neutral fraction from fast-pyrolysis of pine sawdust in accordance with the present invention. The authentic novolak produced main peaks (from deconvolution) at 150, 130 and 120 ppm corresponding to hydroxy-substituted aromatic carbons, respectively. In the aliphatic region, the main peaks were at 35 and 40 ppm, assigned to ortho-para methylene bridges and para-paras methylene bridges, respectively. The presence and intensity of such peaks corresponded to the formation of random novolaks. On substitution of phenol with the phenol/neutral fraction produced in accordance with the present invention, the key peaks of the random novolak remained, but peaks characteristic of the types of phenolic compounds present also appeared such as at 150 ppm (meta-aromatic carbons attached to methoxy groups), 55 ppm (methoxy groups), and 20 ppm aliphatic groups.

Key differences between the authentic novolak and the phenol/neutral-substitued novolak produced from the process of the present invention were in relative peak intensities. While the ratio of unsubstituted meta-aromatic carbons to ortho-para methylene bridges (130 to 35 ppm) in the authentic sample was roughly 7:1, the ratio in the phenol/neutral novolak was approximately 4:1 (60% of the original value). Such a difference was anticipated, since the phenol/neutral novolak of the present invention contained a number of meta substituted methoxy compounds. The phenol-formaldehyde novolak had a

high ratio of hydroxy-substituted aromatic carbons (150 ppm) to unsubstituted meta-aromatic carbons (130 ppm) than the phenol/novolak of the present invention (40% vs 30%). Molding compounds have been made with the novolaks developed with 50% replacement of phenol with the phenol/neutral fractions, and these molding compounds had similar tensile and flexural strength and comparable Izod impact strength. This latter parameter can be controlled by the type filler used. Thus, these tests indicate that novolak resins produced by substituting about 50% of the phenol with the phenol/neutrals fraction produced from the present invention provide acceptable commercial products. With said substitution, between about 25 to 75% by weight of the P/N fraction in replacement of phenol can be used, preferably, between about 35 to 65% can be used. Most preferably, about 50% is used.

EXAMPLE V

Resin Preparation

282.5g of phenol/neutrals derived from a fast-pyrolysis oil obtained from pine sawdust according to the process in Example IV was placed in a reaction container. 312.2g of 90% phenol (aqueous) and 6.0g of concentrated hydrochloric acid were added to the phenol/neutrals fraction. The mixture was heated to about 96°C and 175.7g of 37% formalin was added slowly under constant stirring. During the addition of the first half of the formalin, a brisk exotherm occurred and gradually died down upon continuation of the formalin addition.

After all of the formalin was added, the reaction mixture was kept at 90 to 95°C for an additional hour. The mass was then cooled to 85°C and a solution of 3.34g of sodium carbonate dissolved in 70.0g of water was slowly added under constant stirring. The reaction mass was heated under slowly increasing vacuum until a vacuum of 27 inches was reached at a temperature of 15°C. The vacuum and heating were discontinued and, while still hot, the resulting resin was poured into a cooling pan. After

the resin had cooled to room temperature, it was crushed to produce small pieces for further grinding and processing.

Three 1.25g samples of the resin were ground to a coarse grind by hand in a mortar and pestle and mixed with hexamethylene tetramine and lime (calcium hydroxide) as follows:

	A	B	C
Resin, g	1.25	1.25	1.25
Hexamethylene tetramine,g	0.20	0.26	0.30
Lime,g	0.20	0.23	0.30
Stroke cure, seconds	170	162	150

These stroke cure times are well within commercially acceptable ranges.

Compounding

In preparing the molding compound, a mixture comprising the following materials was made:

Novalak resin	250.0g
Hexamethylene tetramine	37.5g
Lime	25.0g
Zinc stearate	7.5g
Wood flour (filler)	150.0g

The mixture was pebble milled for about 1 hour to a very fine well blended powder and nip rolled a few seconds at 100 to 105°C and sheets were pulled off and cooled. The sheets were broken up into pieces smaller than 1/4" in any dimension and used as molding compounds.

Molding was done in a mold heated to 330°F at a pressure of 6,600 psi to obtain small disc of 1" diameter.

It should be noted that, when the novolak prepared using the P/N fraction of the invention as a

replacement for phenol is cooled to about 110°C (the melt is of a gel consistency that is easily injection moldable) and has a "snap" cure. Both of these properties are highly desirable for injection molding and many other types of commercial applications.

EXAMPLE VI

A novolak was prepared from phenol/neutrals derived from fast-pyrolysis of redwood as feedstock using a similar fractionation step.

The following parts by weight of materials was used in preparing the novolak resin:

P/N Fraction	18.8
88% Phenol	21.3
HCl (Concentrated)	0.42
37% Formaldehyde	11.80
Sodium Carbonate (anhydrous)	1.00
Water	15.00

A mixture of the P/N fraction, phenol and hydrochloric acid was heated to 95-97°C for about 30 minutes. Formaldehyde was added dropwise under constant stirring and the heating was continued on a steam bath for another 30 minutes after the formaldehyde addition was completed. Sodium carbonate dissolved in water was added slowly to achieve neutralization. The resulting resin was washed several times with hot water and the pH of the last wash water was 7.0.

Blends of the resin with hexamethylene tetramine and lime in the following amounts by weight gave the following gel time at 150°C:

Resin	1.25
Hexamethylene Tetramine	0.30
Lime	0.30
150°C gel, seconds	280

EXAMPLE VII

Similar to Example VI, except that pine sawdust was the feedstock, and the gel time was 175 seconds.

It is clear from a comparison of Examples VI and VII that the reactivity of the novolak resin products from this redwood P/N fraction is less than that obtained from the pine sawdust P/N fraction when used under phenolic resin type reaction conditions.

When the fast-pyrolysis oil derived from pine sawdust according to Example IV is fractionated on a continuous basis and the oil flow rate is doubled (20mL/min), the P/N fraction obtained therefrom produces a novolak resin which, when prepared according to Example V, cures at 150°C in 128 seconds.

When the oil flow rate is tripled (30mL/min), the P/N fraction obtained therefrom produces a novolak resin which, when prepared according to Example V, cures at 150°C in 95 seconds. While the exotherms in the double and triple flow rate oil materials are about 115°C (compared to about 108°C for the single flow rate oil materials), it was found that the novolak prepared from the triple flow rate oil material was best in brittleness, was non-caking and glossy and gave better cured resins with much better hot rigidity. Also, it dehydrated easier when compared to standard novolaks (without the P/N fast pyrolysis fraction replacing a portion of the phenol), and this is a processing advantage with much merit under commercial molding conditions.

Similarly, it was found that novolaks wherein up to 50 weight percent of the phenol was replaced with 50% of P/N fractions obtained from fast-pyrolysis oils obtained from Douglas fir bark have much better (shorter) cure times compared with their corresponding pine sawdust derived analogues.

Table III shows test data for molds prepared in which 50% by weight of phenol in a novolak resin is

replaced with a P/N fraction obtained from a fast-pyrolysis oil from pine sawdust.

TABLE III

FLOWS	POWDER PROPERTIES	PHYSICALS	
Small cup ct/wt/15.112	Sp.Gr. 1.340	Izod Impact strength	.251
		Tensile strength	6,000
		Flexure	9,300
		Water absorb.	.56

Brabender 125°C - 253
Low Torque - 550
pH 10.7

While any acid may be used to catalyze the P/N fraction and phenol in preparing the novolak resins, it is preferred to use sulfuric acid, hydrochloric acid, phosphoric acid and oxalic acid. Most preferred, however, is hydrochloric acid and sulfuric acid.

In order to produce a useful novolak resin and/or molding composition containing the P/N fraction from the fast-pyrolysis oil process according to the invention, it has been found that from about 25 to about 75% by weight of the phenol normally used in a phenol-formaldehyde novolak resin can be replaced with the P/N fraction.

With respect to the economic benefits of the present invention, petroleum derived phenol costs about $0.34 (spot price) and $0.40 (list price) per pound. Prior to the present invention, the main competition has been the lignin-derived substitutes from commercial pulping processes. Kraft lignins have to be made chemically more reactive to replace phenol in phenol-formaldehyde resins with similar performance. These commercial products are sold as resin co-reactants, and their price ranges from $0.33-$0.85 per pound depending on the reactivity needed (based on Kraft lignins). Less

expensive products available from the process of the present invention are co-reactants with the ability to replace about 50% of the phenol in phenol-formaldehyde resins as described above. Indications are that for molding compounds and for plywood adhesive resins, a 50% phenol replacement would provide comparable performance to the commercial phenolic adhesives. However, there is a significant cost reduction factor in that the phenol-formaldehyde fractions produced from the phenol/neutral composition of the present invention have an amortized cost projection at approximately $0.16 per pound compared to $0.34-$0.40 per pound for commercial phenol. If the lignocellulosic starting material is bark, this cost is even less because the yield of phenolics from the bark is higher than that of sawdust or pine. Plant sizes were 250 to 1000 tons of feedstock per day, 15% return on capital, plant life of 20 years, and waste sawdust at $10.00 per dry ton.

As described above, the most developed application for the end products of the present invention is the replacement of about 50% and potentially more of the phenol in phenol-formaldehyde resins for use as molding compounds, foundry materials, and shell moldings. Other potential applications for the resulting product of the process of the present invention include the replacement of phenol in softwood and hardwood plywood resins, the insulation market, composite board adhesives, laminated beams, flooring and decking, industrial particle board, wet-formed hard boards, wet-formed insulation boards, structural panel board, and paper overlays. Alternative adhesive systems from the carbohydrate-rich fractions of the present invention could also be made.

In addition, another product that can be derived from the other fractions of the pyrolysis oils is an aromatic gasoline. Passage of vapors of these compounds over zeolite catalysts produces high octane gasoline, as more clearly discussed in "Low-pressure upgrading of

Primary Pyrolysis Oils from Biomass and Organic Waste," in Energy from Biomass and Wastes, Elsevier Applied Science Publishers, London, pp. 801-830 (1986).

A final advantage to the present invention is that about one-third of the usual amount of formaldehyde employed in conventional phenolic adhesives is necessary in producing adhesives wherein 50% of the phenol is substituted with phenol/neutral fractions provided by the present invention. Since there is significant environmental concern over formaldehyde emissions from resins, the products resulting from the process of the present invention therefore become very important from this context.

As can be seen from the above, a novel process for fractionating fast-pyrolysis oils to produce phenol-containing compositions having phenol/neutral fractions contained therein suitable for manufacturing phenol-formaldehyde resins are disclosed. The process is simple and economic, and can be used in either batch or continuous mode operations. The resulting phenol/neutral composition can be subsequently utilized to produce movolaks and resole resins of comparable or superior performance characteristics relative to standard phenol-formaldehyde resins yet the pyrolysis-derived phenolic feedstocks are projected to cost less than half of the cost of petroleum-derived phenol. Moreover, these resulting resins have numerous different types of applications, and the cost benefits alone are significant.

While the foregoing description and illustration of the invention has been shown in detail with reference to preferred embodiments, it is to be understood that the foregoing are exemplary only, and that many changes in the compositions can be made without departing from the spirit and scope of the invention, which is defined by the attached claims.

CLAIMS:

1. An improved process for preparing phenolformaldehyde novolak resins comprising:

replacing a portion of the phenol normally used in making novolak resins with a phenol containing composition/neutral fractions extract obtained by fractionating fast-pyrolysis oils derived from biomass materials as follows:

admixing said oils with an organic solvent having a solubility parameter of approximately 8.4-9.1 polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.8 range;

separating the organic solvent-soluble fraction containing the phenolic compounds/neutral fractions, from said mixture and admixing it with water to extract water-soluble materials therefrom;

separating the organic solvent-soluble fraction from said water fraction and admixing said solvent fraction with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds from said solvent fractions; and

separating the residual organic solvent-soluble fraction and removing the organic solvent therefrom to produce said phenolic compounds/neutral fractions extract; wherein the neutral fractions have molecular weights of between about 100 to about 800, and the phenol containing composition/neutral fractions extract is soluble in an organic solvent having approximately 8.4-9.1$[cal/cm^3]^{1/2}$ with polar components in the 1.8 to 3.0 range and hydrogen bonding components in the 2.4-5 range.

2. The process of claim 1 wherein said fast-pyrolysis oils are produced from lignocellulosic materials.

3. The process of claim 2 wherein said lignocellulosic materials are selected from the group consisting of

softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

4. The process of claim 1 wherein said phenol containing composition/neutral fractions extract replaces at least 75% by weight of the phenol in said phenol-formaldehyde novolak resins.

5. The process of claim 1 wherein said phenol containing composition/neutral fractions extract replaces at least 50% by weight of the phenol in said phenol-formaldehyde novolak resins.

6. The process of claim 1 wherein said phenol containing composition/neutral fractions extract replaces at least 25% by

weight of the phenol in said phenol-formaldehyde novolak resins.

7. A phenol-formaldehyde novolak resin wherein a portion of the phenol normally contained in said resin is replaced by a phenol containing composition/neutral fractions extract obtained by a process of fractionating fast-pyrolysis oils derived from biomass materials as follows:

admixing said oils with an organic solvent having a solubility parameter of approximately 8.4-9.1 polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.8 range;

separating the organic solvent-soluble fraction containing the phenolic compounds/neutral fractions, from said mixture and admixing it with water to extract water-soluble materials therefrom;

separating the organic solvent-soluble fraction from said water fraction and admixing said solvent fraction with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds from said

solvent fractions; and

separating the residual organic solvent-soluble fraction and removing the organic solvent therefrom to produce said phenolic compounds/neutral fractions extract; wherein the neutral fractions have molecular weights of between about 100 to about 800 and the phenol containing composition/neutral fractions extract is soluble in an organic solvent having a solubility parameter of approximately 8.4-9.1 $[cal/cm^3]^{1/2}$ with polar components in the 2-4.5 range.

8. A phenol-formaldehyde novolak resin according to claim 7, wherein said fast-pyrolysis oils are produced from lignocellulosic materials.

9. A phenol-formaldehyde novolak resin according to claim 8, wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

10. A phenol-formaldehyde novolak resin according to claim 7, wherein said phenol containing composition/neutral fractions extract is at least a 75% by weight replacement of the phenol normally contained in said resin.

11. A phenol-formaldehyde novolak resin according to claim 7, wherein said phenol containing composition/neutral fractions extract is at least a 50% by weight replacement of the phenol normally contained in said resin.

12. A phenol-formaldehyde novolak resin according to claim 7, wherein said phenol containing composition/neutral fractions extract is at least a 25% by weight replacement of the phenol normally contained in said resin.

13. A process for preparing a phenol-formaldehyde novolak resin which is susceptible to molding under high

temperatures and pressures comprising grinding the resin of claim 7, and compounding said ground resin with hexamethylene tetramine, lime and filler material.

14. A process according to claim 13, wherein said fast pyrolysis oils are produced from lignocellulosic materials.

15. A process according to claim 14, wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

16. A process according to claim 13, wherein said phenol containing composition/neutral fractions is at least 75% by weight replacement of the phenol normally contained in said resin.

17. A process according to claim 13, wherein said phenol containing composition/neutral fractions extract is at least a 50% by weight replacement of the phenol normally contained in said resin.

18. A process according to claim 13, wherein said phenol containing composition/neutral fractions extract is at least 25% by weight replacement of the phenol normally contained in said resin.

19. A molded composition comprising a phenolformaldehyde novolak resin wherein a portion of the phenol normally contained therein is replaced by a phenol containing composition/neutral fractions extract obtained by a process of fractionating fast-pyrolysis oils derived from biomass materials as follows:

admixing said oils with an organic solvent having a solubility parameter of approximately 8.4-9.1 polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.8 range;

separating the organic solvent-soluble fraction containing the phenolic compounds/neutral fractions, from said mixture and admixing it with water to extract water-soluble materials therefrom;

separating the organic solvent-soluble fraction from said water fraction and admixing said solvent fraction with an aqueous alkali metal bicarbonate solution to extract strong organic acids and highly polar compounds from said solvent fractions; and

separating the residual organic solvent-soluble fraction and removing the organic solvent therefrom to produce said phenolic compounds/neutral fractions extract;

said phenol containing composition/neutral fractions extract having neutral fractions having molecular weights of between 100 to about 800 and the phenol containing composition/neutral fractions extract is soluble in an organic solvent having a solubility parameter of approximately 8.4-9.1 $[cal/cm^3]^{1/2}$ with polar components in the 1.8-3.0 range and hydrogen bonding components in the 2-4.5 range; said molding compound further containing admixed therewith hexamethylene tetramine, lime and a filler material.

20. The phenol-formaldehyde novolak resin molded composition of claim 19, wherein said fast-pyrolysis oils are produced from lignocellulosic materials.

21. The phenol-formaldehyde novolak resin molded composition of claim 20, wherein said lignocellulosic materials are selected from the group consisting of softwoods, hardwoods, pine sawdust, bark, grasses and agricultural residues.

22. The phenol-formaldehyde novolak resin molded composition of claim 19, wherein said phenol containing composition/neutral fractions extract is at least a 75% by weight replacement of the phenol normally contained in said

resin.

23. The phenol-formaldehyde novolak resin molded composition of claim 19, wherein, said phenol containing composition/neutral fractions is at least a 50% by weight replacement of the phenol normally contained in said resin.

24. The phenol-formaldehyde novolak resin molded composition of claim 19, wherein said phenol containing composition/neutral fractions extract is at least a 25% by weight replacement of the phenol normally contained in said resin.

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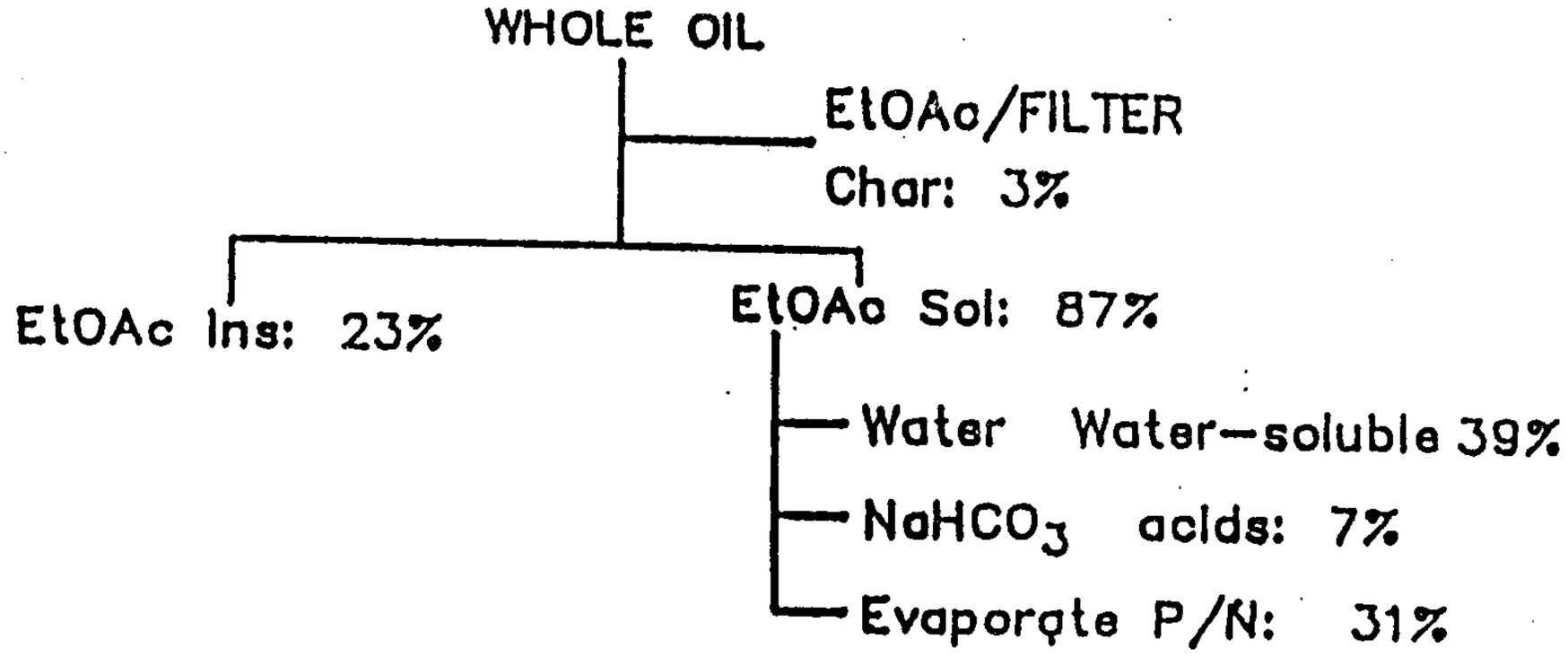

FIG.1