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[54] **FRICTION ELEMENT COMPOSITION**

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[60] Division of Ser. No. 188,596, Oct. 12, 1971, Pat. No. 3,767,612, which is a continuation of Ser. No. 872,737, Oct. 30, 1969, abandoned.

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[58] **Field of Search**..... 260/838, 38, DIG. 39

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[57] **ABSTRACT**

A friction binder for a friction element composition, especially useful where cashew nut shell oil and/or vegetable oils have been used in a phenolic resin composition, may be prepared by blending a non-oxyalkylated resole with resin selected from the group consisting of an oxyalkylated resole, alkylated resole, an oxyalkylated novolac, an alkylated novolac, and mixtures thereof. The friction element composition is prepared by adding to this binder asbestos fiber and friction imparting materials, and curing the resultant material.

4 Claims, No Drawings

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FRICTION ELEMENT COMPOSITION

This is a division of copending application Ser. No. 188,596, filed Oct. 12, 1971, now U.S. Pat. No. 3,767,612, issued oct. 23, 1973; which is a continuation of application Ser. No. 872,737, filed oct. 30, 1969, now abandoned.

This invention relates to a resinous material as a binder for friction elements and more particularly to those elements which are suitable for use in brakes of automotive vehicles, clutch facing, machine brakes and many other industrial applications. It is especially useful where cashew nut shell oil polymerizates or vegetable oil-modified phenolic resin compositions have been used in the past.

Phenol aldehyde, or hydroxy aromatic-aldehyde condensation products having methylol side or end groups are known in the art as "resoles". They are formed from condensing a phenol with an excess of aldehyde and with an alkaline catalyst, also known as "one-stage" resins and are of the thermosetting type. Except when oxyalkylated, they are self setting. That is, upon the application of heat there results the formation of a "resite," which is an infusible three-dimensional polymer.

Phenol aldehyde novolac resins, on the other hand, are phenolended chain polymers. They are formed by the reaction of an aldehyde with an excess of phenol in the presence of an acid catalyst and/or heat. They are thermoplastic, permanently soluble and fusible. However, upon the addition of a curing agent, they can be cured into an insoluble, infusible resin. Thus, novolac resins are known as "two-stage" resins.

Phenol aldehyde condensation products have been used as binders for abrasive materials. However, to our knowledge, the novel phenol aldehyde products of this invention have not been used as binders.

As used herein "friction particle" is intended to mean having the properties of substantially no softening at elevated temperatures and will not flow together or cohere with other particles, as a "friction binder" would, or fuse with like friction particles. It is insoluble, having an acetone extraction of less than 35 percent and often less than 5 percent; it is infusible, i.e., has gone beyond the "B" stage, to the "C" stage. It will not melt at 700°F. A friction particle is held in place with a friction binder.

As used herein, a friction binder has the properties of flowability, and has adhesive and cohesive bonding action and thereby binds together the asbestos and other additives (including a friction particle) necessary for building a brake lining or other similar article of manufacture. The binder, as supplied to the industry, will melt as a dry powder or is a liquid resin, and can be either an A stage or B stage resin. The binder becomes a C stage resin after it is combined with the other ingredients and cured.

The composition of the binder, friction particle and other additives, is heated to between 300°–400°F. and pressed at between 500–2000 pounds per square inch in order to form a brake lining composition, or clutch facing or other braking device.

It has now been found that a composition of matter useful as a friction binder can be prepared by blending hydroxy aromatic hydrocarbon-aldehyde resole with a resin selected from the group consisting of an oxyalkylated hydroxy aromatic hydrocarbon-aldehyde resole, an alkylated hydroxy aromatic hydrocarbon-aldehyde resole, an alkylated hydroxy aromatic hydrocarbon-aldehyde, an oxyalkylated hydroxy aromatic hydrocarbon-aldehyde novolac and mixtures thereof. The first said resole can be alkylated but not oxyalkylated. Among the preferred embodiments of this invention are the following:

1. The blended product of between about 5 and about 40 percent by weight of an oxyalkylated resole with between about 95 and about 60 percent by weight of one or more of
   a. one or more non-oxyalkylated, non-alkylated resoles,
   b. a non-oxyalkylated, alkylated resole,
   c. a mixture of a non-oxyalkylated resole and a non-oxyalkylated, non-alkylated resole,
   d. a mixture of a non-oxyalkylated, non-alkylated resole and a non-oxyalkylated alkylated novolac, and
   e. a mixture of a non-oxyalkylated, non-alkylated novolac and a non-oxyalkylated, non-alkylated resole.

2. The blended product of between about 95 and about 60 percent by weight of a non-oxyalkylated, non-alkylated resole with between about 5 and about 40 percent by weight of one or more of
   a. an oxyalkylated novolac, and
   b. a non-oxyalkylated, alkylated resole.

3. The blended product of between about 5 and about 40 percent by weight of an oxyalkylated novolac with between about 95 and about 60 percent by weight of one or more of
   a. two or more non-oxyalkylated, non-alkylated resoles,
   b. an alkylated resole,
   c. a mixture of an alkylated resole and a non-oxyalkylated, non-alkylated resole,
   d. a mixture of a non-oxyalkylated, non-alkylated resole and a non-oxyalkylated alkylated novolac, and
   e. a mixture of a non-oxyalkylated, non-alkylated resole and a non-oxyalkylated, non-alkylated novolac.

4. The blended product of between about 5 and about 95 percent by weight of a solid, B-stage, non-oxyalkylated, alkylated resole, with between about 95 and about 5 percent by weight of a liquid, A-stage non-oxyalkylated, alkylated resole.

In general, an oxyalkylated hydroxy aromatic material, whether it is a novolac or a resole, will not react with a novolac by itself. The methylol groups on a resole are believed to be needed to react with the polyol groups of the oxyalkylated materials.

The friction binder is formed by blending the resole with the novolac, or other resole. Usually, the resole and oxyalkylated resole or oxyalkylated novolac are both liquids, so blending is easily achieved. However, when one is a solid, it is powdered and mixed with the liquid. When both are solids, both are dry blended such as by ball milling together. Then they are mechanically blended, such as by being passed through a hammer mill equipped with a quarter mesh screen.

Normally, the materials are not reacted together. However, in some cases, it may be desirable to partially react the blended mixture to increase its viscosity. The temperature chosen should be within the limits of relatively easy reaction control and will normally be from about 150° to 210°F. The resultant material is normally in the A stage of polymerization. However, in some

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cases, the oxyalkylated resole or oxyalkylated novolac in combination with a resole and a novolac is reacted and carried to a B stage condition. This reacted B stage blend can be used by itself or in combination with a formaldehyde donor, such as hexamethylenetetramine, as a binder. The blend is suitable for use as a friction composition constituent and as a binder for brake lining fillers.

Examples of phenols which can be used in preparing a phenol aldehyde resole or novolac for use in practicing the invention include ortho-, para- directing hydroxy or amine aromatic compounds having 6 to 24 carbon atoms such as phenol itself (C_6H_5OH), naphthol, anthranol and substituted derivatives thereof where the substituents on the aromatic compound are independently selected from H, Cl, Br, F, NH_2 and

a. alkyl groups or radicals of 1 to 60 carbon atoms, preferably of 1 to 30 carbon atoms, and their various isomeric forms and substituted on the aromatic nucleus in the ortho- or para- position;
b. cycloalkyl groups of 5 to 12 carbon atoms such as cyclohexyl, cyclopentyl, methylcyclohexyl, butylcyclohexyl, and the like;
c. alkyl, aryl and cycloalkyl ketonic groups wherein the hydrocarbon portion is as defined above in (a) and (b);
d. alkyl, aryl and cycloalkyl carboxylic groups wherein the hydrocarbon part is defined as above in (a) and (b);
e. aryl groups of 6 to 24 carbon atoms such as phenyl, naphthyl, anthryl, and the like;
f. aryl substituted alkyl wherein the aryl is phenyl which may contain lower alkyl and/or hydroxy substituents so that the resulting hydroxy aromatic is, for example, a bisphenol; and
g. mixtures of the aforesaid hydroxy aromatics.

Suitable substituted phenols include the following: para-phenyl phenol, para-benzyl phenol, para-beta-naphthyl phenol, cetyl phenol, para-cumyl-phenol, para-tert-butyl phenol, sec-butyl phenol, para-tert-amyl phenol, para-tert-hexyl phenol, para-alpha-naphthyl phenol, para-hydroxyacetophenone, para-hydroxybenzophenone, para-isooctyl phenol, para-tert-octyl phenol, para-cyclohexyl phenol, para-d-limonene phenol, para-l-limonene phenol, a phenol alkylated with oleic acid, such as phenol alkylated with oleic acid, para-decyl phenol, para-dodecyl phenol, para-tert-decyl phenol, butyl naphthol, amyl anthranol, para-nonyl phenol, para-methyl phenol, bisphenols such as para,para'-isopropylidene diphenol, para,para'-methylene diphenol, as well as the corresponding ortho-derivatives of the previously mentioned compounds such as ortho-butyl phenol and ortho-nonyl phenol as well as mixtures thereof, and aniline.

Mixtures of various hydroxy aromatic compounds mentioned herein also may be used.

Included among the phenolic reactants which may be used are those known as the "cresylic acids" and these often comprise a heterogeneous mixture of having two reacting hydrogen positions on each of them; that is, compounds unsubstituted in the ortho- and para- positions, of the molecule, to compounds that only have one functional position, and hence, relatively unreactive. These compounds may include the following: 3,5-xylenol, m-cresol, 3,4-xylenol, 2,5-xylenol, 2,3-xylenol, phenol, p-cresol, orthocresol, 2,4-xylenol, and 2,6-xylenol. Cresylic acids or tar acids are generally applied to phenol and its homologs which may include cresols, xylenols, trimethyl phenols, ethyl phenols, and higher boiling materials such as dihydroxy phenols, polycyclic phenols and the like. They are often obtained by a low-temperature trimerization of coal, lignite, and the like, or a conventional high-temperature coke oven tar, or the liquid product of petroleum cracking both thermo and catalytic, shell oil, coal hydric hydrogenation products, and the like.

Polyhydroxy aromatic reactants, such as resorcinol, may also be used.

Particularly useful in this invention are mixtures of aniline and phenol to react with an aldehyde or ketone to produce either a novolac or a resole, depending on the other conditions described above.

Also useful in the invention are mixtures of urea and phenol to react with the aldehyde or ketone to produce either a novolac or a resole depending on the other conditions described above.

Among the aldehydes which may be used within the scope of this invention to produce either the resole or the novolac, are formaldehyde or any of its variations, such as 37 percent formalin concentration or para-aldehyde acetaldehyde, propionaldehyde, isobutyraldehyde, isopentaldehyde, and the like. The aldehyde should have not more than 8 carbon atoms and should not detrimentally affect the resinification or oxyalkylation of the resin. Preferred aldehydes are those having from 1 to 4 carbon atoms, such as formaldehyde, which may be in aqueous solution (37 percent), or in any of its low polymeric forms such as paraform or trioxane. Other aldehydes include para-aldehydes, furfural, 2-ethyl-hexanal, ethylbutyraldehyde, heptaldyde and glyoxal, benzaldehyde and crotonaldehyde.

NOVOLACS

To prepare a novolac, the proportion of aldehyde to be condensed with the hydroxy aromatic compound may be varied in order to obtain different molecular weights, and the viscosity of the finished resin may be controlled by the mole weight of the novolac; preferably the proportion of aldehyde employed is from 0.5 to 1.0 per mole of the hydroxy aromatic compound.

Among the substituted phenols which may be used to prepare the novolacs for this invention are those substituted with long-chain ethylenically unsaturated hydrocarbons, such as the linseed-type oils. However, it is within the scope of this invention to employ any animal and/or vegetable oil which achieves the objects of this invention based on the similarity in properties with the long-chain hydrocarbon oils. Such oils would be positioned on the phenol in the ortho- or para- positions, and preferably in the para- position. Many of them are similar in properties to linseed oil having non-conjugated unsaturation of at least 50 iodine number, and have sufficient compatibility with the novolac after it is polymerized. Safflower oil is typical of these oils. It may be in the form of a glycerol ester of the fatty acids wherein the fatty acids are of a composition comprising more than 40 percent by weight of linolenic acid. The remaining percentages of fatty acid can be any saturated or ethylenically unsaturated fatty acid having 12 to 22 carbon atoms and more preferably oleic and linolenic acid so that the fatty esters have an iodine number of at least 50. The iodine value (iodine number) is a measure of unsaturation, and is defined as the number of grams of iodine required per 100 grams

of unsaturated material to obtain the saturated material. In addition to the preferred glycerol ester, other polyhydric alcohols can be reacted with the described fatty acids to produce a low acid number ester of a polyol having 2 or more hydroxyl groups. Typical polyols include ethylene glycol, diethylene glycol, pentaerythritol, dipentaerythritol, sorbitol and the other polyhydric alcohols.

The acid catalyst to be used when preparing the novolacs to be used in this invention may be chosen from oxalic acid, sulfuric acid, hydrochloric acid and other strong acids used in the art for preparing novolacs. In addition, wetting agents of the anionic type, such as sodium alkylaryl sulfonates, are also useful as secondary catalysts in preparing novolacs.

The two-stage resins are curable by reaction with hexamethylene tetramine to form dibenzyl and tribenzyl amines, as well as hexatriphenol. One may also use ammonium hydroxide, which reacts with the formaldehyde to form hexamethylene tetramine. Other amines may also be used, such as ethylene diamine or ethylene triamine, or methylamines, etc. These can be used to react with formaldehyde to form a composition similar to hexamethylene tetramine. The resulting compound would be an aldehyde donor.

The phenol aldehyde novolac type resin is prepared by charging the desired phenol and aldehyde raw materials and catalysts to a reaction vessel. The reaction begins at about 100°C and proceeds under temperatures up to about 200°C, at any pressure up to about 100 lbs/square inch gauge for about 1½ hours, or until the desired degree of polymerization has taken place. Thereafter, the catalyst is neutralized where necessary, and the excess reactant, water, and other materials are taken off by dehydration and the molten resin is discharged from the vessel. It has been found that a novolac which has not been neutralized and is stable will cure more rapidly with a resole than a novolac which has been neutralized.

From the foregoing, it is apparent that many hydroxy aromatic compounds may be used in practicing the present invention to provide a novolac which can be then reacted with an hydroxy aromatic aldehyde resole to form the friction particle of this invention, provided the aromatic hydroxyl group is reactive and the hydroxy aromatic compound is capable of reacting with an aldehyde or a mixture of aldehydes to produce a novolac condensate. Pure, refined phenols may be used, but this is not necessary. For instance, phenols may be alkylated and then may be reacted in crude form with an aldehyde. In such crude form, the phenols may contain some polyalkylated, as well as non-alkylated, phenols.

The process for alkylation of a phenol is well known in the art. First, dehydration (of water) is carried out with vacuum at elevated temperatures, for instance, between about 100 and about 150 degrees centigrade under a vacuum of between about 20 and about 30 inches of mercury. Then, the dehydrated phenolic material is acidified to a pH of between about 1 and about 5 with H_2SO_4 or in some cases BF_3. Following this, a terpene or vegetable oil is added and the reaction mixture heated to between about 80° and about 140°C at atmospheric pressure. The molar ratio of reactants is between about 0.1 mole of terpene or vegetable oil per mole of phenol to about 2.5 mole of terpene or vegetable oil per mole of phenol. When tung oil is employed as a vegetable oil in the alkylation, use of BF_3 to acidify would cause gelation, so it is not used, but H_2SO_4 can be used.

The proportion of aldehyde to be condensed with the hydroxy aromatic compound to form a precondensate may be varied to prepare novolacs of different molecular weights. Viscosity of the finished precondensate may be controlled by the mole weight of the novolac. Preferably, the proportion of aldehyde employed varies from about 0.5 to 1.0 mole per mole of phenol when a mono- or difunctional phenol is used. In instances where a trifunctional phenol is used, i.e., unsubstituted in the ortho- and para- positions, a preferred upper limit of the aldehyde may be about 0.70 mole of aldehyde per mole of phenol so as to minimize the formation of insoluble, infusible condensates. It is preferred that the aldehyde and phenol be condensed using an acid catalyst to shorten the time required for complete condensation of the reactants. Suitable acid catalysts include sulfuric acid, hydrochloric acid, and oxalic acid. These catalysts are generally employed employed in the amount of 0.1 to about 5 percent by weight of phenol to be condensed.

Where a mixed aldehyde phenol-aldehyde precondensate is to be prepared, it is formulated by charging the desired phenol and aldehyde raw materials and catalysts to a reaction vessel. The reaction proceeds under temperatures from about 25° to about 150°C at a pressure from about ambient up to about 100 pounds per square inch gauge pressure for a period of time from about 5 minutes to about 5 hours, a suitable time being about 1½ hours, or until the desired degree of condensation has taken place. The phenol is first reacted with the longer-chain aldehyde to form a phenol-longer chain aldehyde precondensate, followed by a second-step reaction of the phenol-longer chain aldehyde precondensate with formaldehyde to form a thermosettable phenol aldehyde precondensate material. In the second step, the reactants are refluxed at atmospheric pressure, although higher reflux temperatures up to about 150°C can be used by employing elevated pressure. The formaldehyde can be added all at once in the second step, or added gradually. If the formaldehyde is added all at once, then a temperature range between about 50° and about 60° is used at the beginning of the second-step reaction, until the exothermic reaction subsides, and then the temperature is increased slowly to between about 70° and about 80°C and held until further exothermic reaction subsides, and then the reaction mixture is heated to reflux temperature which is about 100 degrees centigrade at atmospheric pressure. If elevated pressure is used, then the reflux temperature can be increased to as high as about 140°C. If the formaldehyde is added gradually in the second step, then a temperature range between about 95° and about 140°C can be used. The catalyst is then neutralized and the excess reactant, water and other materials are taken off.

While the precondensate is still at an elevated temperature, from about 25° to about 150°C, but below the boiling point of the resultant solution or suspension, with about 100°C being very suitable, it may be reduced in viscosity by addition of suitable solvent. The amount of solvent may vary from about 10 to 70 percent of the precondensate by weight and a suitable ratio of precondensate to solvent is about 10 parts of precondensate to 9 parts of solvent. The controlling

factor is the resulting viscosity of the precondensate prepared, rather than the actual volume of solvent charged. Among the solvents which may be used for this purpose are ethanol, methanol, toluene, xylene, ketones, such as acetone, and methylethyl ketone, and mixtures of aromatic and aliphatic hydrocarbons, such as mixtures of benzene and mineral spirits, or benzene and acetone.

OXYALKYLATION

Oxyalkylated resins are prepared which preferably contain substantially no free reactive hydroxy aromatic groups, for example, less than about 0.5 percent of the aromatic hydroxyl present originally in the hydroxy aromatic or hydroxy aromatic aldehyde condensate. To remove the aromatic hydroxys, the hydroxy aromatic aldehyde resin can be reacted with a compound which etherifies the aromatic hydroxyl groups so that almost all of the aromatic hydroxy groups present in each hydroxy aromatic aldehyde condensate unit are so reacted.

The preferred method of hydroxyalkylation is by reaction with compounds containing a mono-oxirane ring. Such compounds include ethylene oxide, propylene oxide, butylene oxide, styrene oxide and cyclohexane oxide, glycidol and epichlorohydrin. Many other monoepoxides can be used, but the alkylene oxides containing not more than 6 carbons are generally preferred. Additional useful compounds are phenyl glycidyl ether and related compounds prepared from the reaction of epichlorohydrin and monofunctional alkylated and halogenated phenols such as pentachlorophenyl glycidyl ether.

Catalysts for the reaction of the oxirane ring compounds and phenolic hydroxyl groups may be alkali or alkaline earth hydroxides, primary amines, secondary amines, tertiary amines or basic alkali salts. These include sodium, potassium, lithium, calcium and barium hydroxides, amines such as methyl, dimethyl, diethyl, trimethyl, triethyl, tripropyl, dimethyl benzyl, dimethyl hydroxyethyl, dimethyl-2-hydroxypropyl and the like, and salts of strong bases and weak acids such as sodium acetate and benzoate.

The reaction may be carried out at temperatures of about room temperature to 250°C, and preferably in the absence of solvents, although solvents may be used to reduce viscosity when desired. When oxyalkylating resoles, the reaction should be carried out at lower temperatures than when oxyalkylating novolacs, because there is a possibility that reaction of the methylol groups with other methylol groups gives methylene linkages, formaldehyde and gelation. When oxyalkylating a novolac, temperatures between room temperature and about 200°C can be used. When oxyalkylating a resole, temperatures between room temperature and about 100°C may be used.

The aromatic hydroxyl of the novolacs may also be hydroxyalkylated by reacting alkylene halohydrins with the aromatic hydroxyl using equivalent amounts of an alkali metal hydroxide to bring about the reaction. Suitable alkylene halohydrins are ethylene chloro- and bromohydrins, propylene chloro- and bromohydrins, 2,3-butylene chloro- and bromohydrins, and glyceryl chloro- and bromohydrins.

Another method for hydroxyalkylating novolacs is reaction with alkylene carbonates such as ethyiene carbonate and propylene carbonate, using a catalyst such as potassium carbonate.

At least one mole of alkylene oxide or other etherifying or esterifying agent is required per mole of aromatic hydroxyl. However, resins prepared by reaction with up to 7 moles of alkylene oxides per mole of phenolic hydroxyl have been found to be useful.

RESOLES

The liquid one-stage resin (resole) which forms a part of this invention may be formed by reacting an hydroxy aromatic compound with an excess of formaldehyde in alkali such as sodium hydroxide dissolved in water. The reaction mixture is gradually heated to reflux and held at reflux until less than about 1 percent of free formaldehyde remains. This provides a preferred reaction product which has less than 2 percent of the formaldehyde unreacted, although this is not critical in this process. Less than 2 percent free CH_2O is desirable. The reaction mixture is then cooled and the catalyst neutralized with some acid such as glacial acetic acid and the pH is adjusted to roughly 6 to 7.5. The reaction mixture may be then further reacted with hexamethylene tetramine or some other aldehyde donor, i.e., curing agent. The resin is then dehydrated to between about 50 to 95 percent solids, and preferably between about 81 to 85 percent solids.

The alkaline catalyst used in preparing the resoles to be used in this invention may be any of those known in the art; for instance, sodium hydroxide and calcium hydroxide. In general, the alkali metal hydroxides and the alkaline earth metal hydroxides and ammonium hydroxide and the amines such as triethanol amines may be used.

Following the intercondensation reaction to form a resole, a stoichiometric quantity of a strong acid such as sulfuric acid, hydrochloric acid, phosphoric acid or oxalic acid, or the like, is added to the reaction mixture in order to neutralize the alkaline condensation catalyst. Sulfuric acid is conveniently employed to neutralize a sodium hydroxide catalyst. The alkaline catalyst may also be neutralized by dilution through repeated washing, however, it is preferred to use an acid. The final resin should have a pH between about 5.5 and 7.5 for good stability.

The hydroxy aromatic compound employed in a resole can be alkylated, if desired, with alkyl groups containing 1 to 12 carbon atoms, or with unsaturated groups, including the long-chain unsaturated vegetable or animal oils, to form alkylated hydroxy aromatic compounds that when reacted with an aldehyde form "heat reactive" resoles. These include alkylene groups of 2 to 36 carbon atoms, fatty acids, polyethers, alkyl ethers, polyesters and polyols and mixtures of these.

Among the high molecular weight or polymeric materials containing aliphatic carbon-to-carbon unsaturation, there are included such naturally occurring materials as unsaturated vegetable, fish or animal oils such as linseed, soya, tung, sesame, sunflower, cotton seed, herring, menhaden, and sardine oils, etc., or chemically modified naturally occurring materials such as allyl ethers of starch, cellulose, or acrylate esters thereof, etc., synthetic drying oils, polymers obtained by polyetherification of such unsaturated compounds such as maleic, fumaric, itaconic, aconitic, chloromaleic, dimerized fatty acids, anhydrides or acids from allyl glycerol, methallyl glycerol ether, glycerol monoacrylate,

butene diol, pentene diol, or polymers obtained by polyetherification of the unsaturated polyols. Other oils include castor oil, tail oil, oiticica oil, safflower oil, and the like, oleic and linolenic acids. These fatty acids have from 12 to 22 carbon atoms. They are often in combination as a glycerol ester or in combination with other polyhydric alcohols or polyols such as ethylene glycol, diethylene glycol, pentaerythritol, dipentaerythritol, sorbitol, and the like polyhydric alcohols.

The blending of the resole with the other components in accordance with this invention can be in various proportions depending upon the ultimate properties desired in the friction binder to be produced, but will generally be in the range of about 50 to about 95 weight percent of the non-oxyalkylated resole based on the total weight of resin components.

It is to be understood that the oxyalkylated resole or oxyalkylated novolac described herein will not be a friction binder along unless blended with a non-oxyalkylated, non-alkylated resole resin or with a non-oxyalkylated, alkylated resole resin. The oxyalkylated resole product is a liquid and will not cure. The preferred compositions of the invention contain at least one of an oxyalkylated resole and an oxyalkylated novolac in combination with the non-oxyalkylated resole.

The friction binder of this invention may be used alone or with other friction binder materials known in the art.

A typical friction element contains about 30 to 60 weight percent asbestos fiber, up to 40 weight percent other inorganic filler and abrasives, about 5 to 15 weight percent organic filler and about 15 to about 30 weight percent binder, including the binder of this invention; all percents are by weight of total composition. Asbestos fiber, abrasive materials and filler materials are charged into a mixer followed by the addition of the binder. The components are kneaded until the fiber, abrasives, and any fillers are thoroughly wetted and a uniform mass is obtained. The mass is discharged from the mixer, rolled out into sheets or extruded or pressure molded and dried, after which it is ready for further processing into friction elements. When the blend is in a B stage condition of polymerization, and powdered, it is mixed with the asbestos and other additives, pressed together in a hot molding operation at approximately 1000 psi. at a mold temperature from about 300°–350°F and then cured.

The abrasives, that is, the friction imparting agents and fillers employed within the scope of this invention include, but are not limited to brass chips, metal shavings and filings, silica, talc, wood flour, chalk, clay, mica, fiber glass, felt, carbon black, graphite metal nitrides and oxides, ground cashew nut shell oil polymerizate, and the friction particle disclosed in Ser. No. 872,753 filed Oct. 30, 1969. These abrasives and fillers can be used to achieve the particular amount of bulk and coefficient of friction desired. The above listed materials have a particle size such that they will pass through a U.S. Standard Sieve (1940) Number 3 which has a sieve opening of 6.3 millimeters. Preferably, the particle size of these materials will range from passing through a Number 4 sieve, sieve opening size 4.76 millimeters, and yet be retained on a Number 100 sieve, sieve opening size 0.140 millimeter.

The following Examples are given to further illustrate the invention. Unless otherwise indicated, all parts are by weight and temperatures in degrees centigrade.

EXAMPLE 1

Part A (the resole)

A reaction vessel is charged with 100 parts of phenol, 120 parts of formelin (37 percent formaldehyde) and 2 parts of flake caustic dissolved in 4 parts of water. This reaction mixture is heated gradually to 60°C and held at 60°C until there is less than 3 percent free formaldehyde and cooled to 30°C, after which 5.5 parts of lactic acid diluted with 5.5 parts of water is added which neutralizes this composition to a pH of 5.5–6.5. After the pH range is achieved, the resin is dehydrated to 59–63 percent solids and cooled to room temperature. The resultant product is a low viscosity liquid, and is identified in Table II as resin Rd.

Part B (the oxyalkylated novolac)

The oxyalkylated novolac can also be referred to as a polyol of a novolac which is oxyethylated, using from about one mole to about 7 moles of ethylene oxide to 1 mole of phenol, depending on the properties desired. For this example, a resin was used with a ratio of 2 moles of ethylene oxide to one mole of phenol.

A typical modified phenol-aldehyde condensation product is prepared by introducing 3,000 parts phenol, 13 parts of oxalic acid catalyst and 6 parts of a wetting agent of Nacconol (sodium alkylaryl sulfonate) into a jacketed reactor and heating to 100°C. (The anionic wetting agents of alkylaryl sulfonate type are preferred.) Then 1,110 parts of a 37 percent aqueous formaldehyde solution are added to the reactor at a rate that the heat of reaction provides a vigorous reflux. Refluxing is continued for 2 hours after the completion of the formalin addition. The reactor contents are dehydrated at 180°C and then dephenolated at 200°C at 50 millimeters vacuum. Approximately 2,030 parts of phenol-aldehyde condensate are produced. Then 7.2 parts of sodium hydroxide are introduced to the reactor. Ethylene oxide is then added to the reactor as either a vapor or a liquid. The reactor temperature is maintained at 190°C for the initial 2 hours and is then permitted to increase to the range of 200° to 220°C until the addition of 878 parts of ethylene oxide is complete. The resulting condensation product has a hydroxyl number of 370, and a Gardner viscosity at 50°C of about 2,000 seconds, and is identified as resin Nc in Table III.

A novel friction binder of the invention was made by blending 60 parts of Part A with 40 parts of Part B. The friction binder was used in formulating a mixture comprising 80 parts of dry mix, and 0.6 part water as follows. The dry mix was composed of 62.5 parts by weight of asbestos shorts, Quebec Standard Asbestos Grade 7K, 12.5 parts by weight of Cardolite friction particles, and 25 parts of barytes abrasive filler. The moisture content of the dry mix was held low between 0.75 and 1.0 percent to avoid any possibility of blistering of the element during cure.

The dry mix was charged to an internal mixer equipped with a Sigma-type blade. The dry materials were mixed and blended for 5 minutes. Then 20 parts of the above-described friction binder were added and mixed for 1 hour until the mass was uniform. The dough-like mix was then discharged from the mixer and charged to an extruder. The extruder was equipped with a 2 inch by ¼-inch rectangular die and had an applied ram pressure of 100 to 300 pounds per square

inch. The dough-like mix was then extruded in a shape which was satisfactory for brake linings. The extruded linings were oven dried for 16 hours at 120°F. The linings were then cut to proper length, reheated for 2 to 3 minutes at about 325°F, bent or arched to the desired curvature and placed into forms (i.e., molds) for curing. These linings were then cured for 8 hours at about 350°F. The cured linings after cooling were expanded to the proper size for mounting into brake shoes. The resulting friction elements were found to be satisfactory for use on automobile brakes.

EXAMPLE 2

70 parts of Part A and 30 parts of Part B of Example 1 were blended. The resulting friction binder was then made up into a brake lining by adding sufficient amounts of the resin blend to give 20 parts of solid resin after curing, 50 parts asbestos fibers, 10 parts Cardolite friction particle, and 20 parts barytes abrasive filler. The resulting mix was extruded to form a drum-type brake lining, which was then dried for 16 hours at 120°F and cured for 8 hours at 350°F. The cured brake lining was tested and found to have a Rockwell hardness of 33M at room temperature which is satisfactory in commercial practice. The lining was heated at 500°F for 15 minutes and had retained a Rockwell hardness of 43L, indicating that the composition retained strength and hardness at elevated temperature.

EXAMPLES 3 to 15

The procedure of Example 2 was repeated to produce additional drum-type brake linings using various proportions of resoles and novolacs for which the formulations are shown in Tables II and III. In Table I are shown the proportions of the indicated resins used to make the resin binders, the Rockwell hardnesses of the cured brake linings as prepared and after heating at 500°F for 15 minutes.

TABLE I

Ex. No.	Resole Formulation	Novolac Formulation	Oxyalkylation Formulation	Resin Ratio	Rockwell Hardness of Brake Lining	
					As Prepared	After 15 minutes at 500°F
1	Rd	—	Nc	60/40	76M	20L
2	Rd	—	Nc	70/30	33M	43L
3	Rd	—	Rc	70/30	56M	13M
4	Ra	—	Rc	70/30	22R	34J
5	Ra-Rd	—	Rc	35/35/30	27M	21L
6	Ra-Rd	—	—	50/50	30M	36L
7	Rd	Nb	Rc	60/20/20	62L	54R
8	Ra	—	Nc	70/30	21R	60J
9	Ra-Rd	—	Nc	35/35/30	36M	18L
10	Rd	Na	Nc	60/10/30	78M	38L
11	Rd	Nb	Nc	60/10/30	12M	25L
12	Ra	Na	—	80/20	67L	81R
13	Ra-Rb	—	—	90/10	—	—
14	Ra	Nb	—	90/10	—	—
15	Ra-Rd	Nb	—	45/45/10	63L	85R

TABLE II

Raw Material:	Resole Resin Formulation			
Resin	a	b	c[1]	d
Phenol	19.93	—	24.43	42.37
Formaldehyde (37.2%)	29.00	24.45	43.98	50.84
Alcohol	28.90	—	—	—
Ammoniacal Liquor	2.43	—	—	—
Para-Tertiary Octyl Phenol	19.93	—	—	—
Caustic Soda	—	2.14	—	0.85
Oxalic Acid	—	0.02	—	—
Para-Tertiary Butyl Phenol	—	21.60	—	—
Sulfuric Acid	—	2.76	—	—
Water	—	27.77	—	3.82
Xylene	—	21.21	—	—
Phosphoric Acid	—	—	0.15	—
Propylene Oxide	—	—	29.68	—
Triethylamine	—	—	1.76	—
Lactic Acid	—	—	—	2.12

[1]In Resole Rc the phenol, formaldehyde, and 2.5 parts of triethylamine were first reacted. This product was then oxypropylated with the remaining specified ingredients.

TABLE III

Raw Material:	Novolac Resin Formulations		
Resin	a	b	c
Phenol	58.45	—	45.85
Formaldehyde (37.2%)	40.62	22.92	16.98
Para-Tertiary Octyl Phenol	—	73.95	—
Sodium Alkylaryl Sulfonate	.01	0.06	0.01
Oxalic Acid	0.03	0.74	—
Water	0.59	—	—
Ammoniacol Liquor	—	2.31	—
Butyl Acid Phosphate	—	—	0.02
Caustic Soda	—	—	0.01
Ethylene Oxide	—	—	36.68
Maleic Anhydride	—	—	0.02

EXAMPLE 16

3000 parts of asbestos fiber, 750 parts barytes abrasive filler, 250 parts of Cardolite friction particle and 1000 parts of the resin binder of Example 2 were mixed

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in a sigma blade mixer to produce a granular mixture. The resulting mixture was charged into a mold and cold pressed at 1000–3000 pounds per square inch to form a disc brake pad. The molded pad was stripped from the mold and cured in a circulating air oven by raising the temperature gradually from room temperature to 350°F over a period of 8 hours, followed by holding the temperature at 350°F for 8 hours.

EXAMPLE 17

The procedure of Example 15 was repeated except that the friction particle was prepared in accordance with Example 2 of copending application Ser. No. 872,753, filed on even date herewith.

Various changes and modifications can be made in the products of this invention without departing from the spirit and scope thereof. The various embodiments of the invention disclosed herein serve to further illustrate the invention but are not intended to limit it.

We claim:

1. A friction element composition comprising a friction imparting abrasive agent, an inorganic filler and a binder composition consisting essentially of at least 60 percent by weight of a non-hydroxyalkylated hydroxy aromatic hydrocarbon-aldehyde resole containing substantially no etherified aromatic hydroxyl groups and at least 10 percent by weight of a non-hydroxyalkylated, alkylated hydroxy aromatic hydrocarbon-aldehyde novolac, wherein the alkylated groups are selected from the group consisting of:

a. alkyl groups of 1 to 60 carbon atoms,
b. cycloalkyl groups of 5 to 12 carbon atoms,
c. alkyl, aryl and cycloalkyl ketonic groups wherein the hydrocarbon portion is as defined in (a) and (b),
d. alkyl, aryl and cycloalkyl carboxylic groups wherein the hydrocarbon portion is as defined in (a) and (b),
e. aryl groups of 6 to 24 carbon atoms, and
f. aryl substituted alkyl wherein the aryl is phenyl, lower alkyl-substituted phenyl or hydroxy substituted phenyl.

2. The composition of claim **1** wherein the first said resole is the condensation product of phenol and formaldehyde in an alkaline medium.

3. The composition of claim **1** wherein the novolac is the condensation product of phenol and formaldehyde in an acid medium.

4. A friction element composition comprising about 30 to 60 weight percent of asbestos fiber, up to about 55 weight percent other fillers and friction imparting abrasive agents, and about 15 to about 30 weight percent of a binder composition consisting essentially of at least 60 percent of a non-hydroxyalkylated hydroxy aromatic hydrocarbon-aldehyde resole containing substantially no etherified aromatic hydroxyl groups and at least 10 percent by weight of a non-hydroxyalkylated alkylated hydroxy aromatic hydrocarbonaldehyde novolac, wherein the alkylated groups are selected from the group consisting of:

a. alkyl groups of 1 to 60 carbon atoms,
b. cycloalkyl groups of 5 to 12 carbon atoms,
c. alkyl, aryl, and cycloalkyl ketonic groups wherein the hydrocarbon portion is as defined in (a) and (b),
d. alkyl, aryl and cycloalkyl carboxylic groups wherein the hydrocarbon portion is as defined in (a) and (b),
e. aryl groups of 6 to 24 carbon atoms, and
f. aryl substituted alkyl wherein the aryl is phenyl, lower alkyl-substituted phenyl or hydroxy substituted phenyl.

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