May 31, 1949. H. H. LEBACH 2,471,631

FURFURYL ALCOHOL-PHENOL ALDEHYDE RESINOUS PRODUCTS AND METHOD OF MAKING THE SAME

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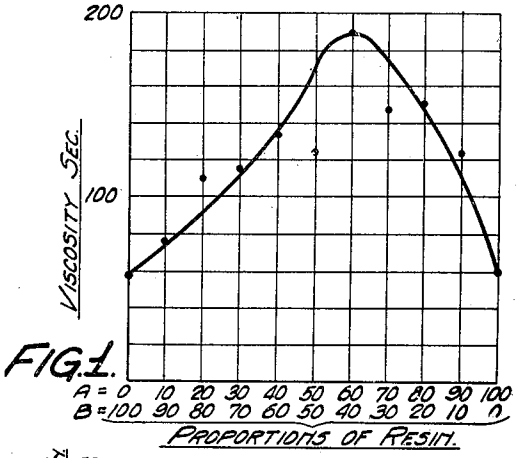

FIG. 1.

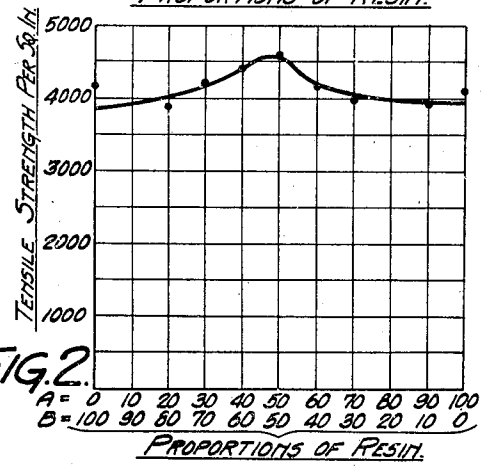

FIG. 2.

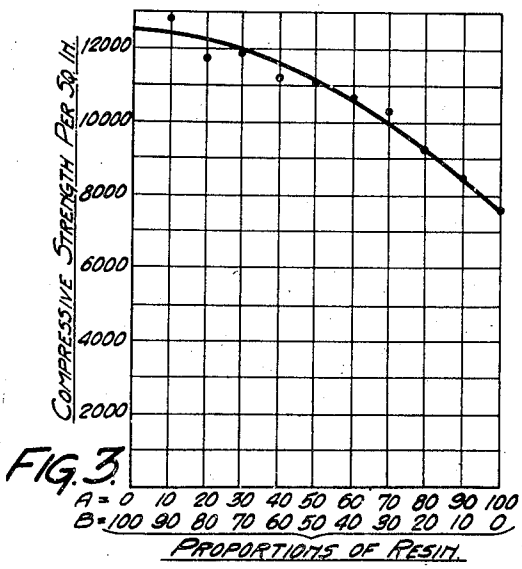

FIG. 3.

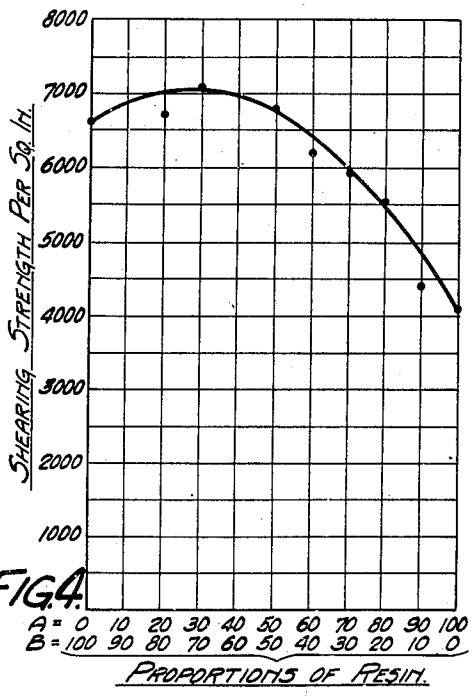

FIG. 4.

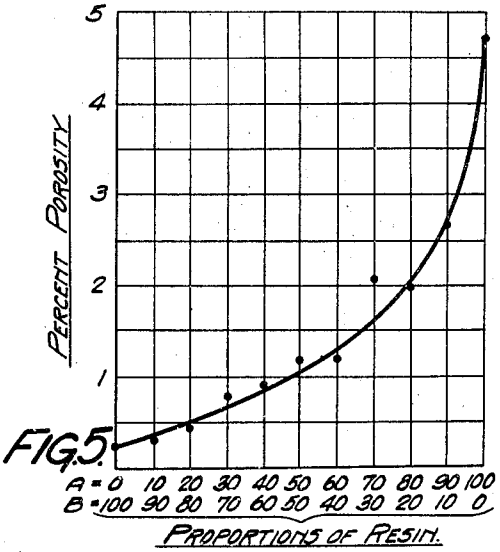

FIG. 5.

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2,471,631

FURFURYL ALCOHOL-PHENOL ALDEHYDE RESINOUS PRODUCTS AND METHOD OF MAKING THE SAME

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Application September 7, 1944, Serial No. 553,074

4 Claims. (Cl. 260—43)

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The present invention relates to novel resinous compositions, both in the initial, convertible, and in the final converted state of reaction, and to the method of preparing the same, and, more particularly, it relates to the production of resinous compositions comprising a phenol-aldehyde resin and resin, obtained by the condensation of furfuryl alcohol or a mixture of furfuryl alcohol and not more than about 15% of furfural. For convenience hereafter, reference will be made merely to the phenol-aldehyde and the furfuryl alcohol condensation products.

Phenolic resins, such as phenol-formaldehyde resins, and compositions made therefrom, have been manufactured for years in large volume and have possessed satisfactory properties for many purposes and are relatively inexpensive, both from the standpoint of raw materials and of manufacturing costs. They have, however, certain inherent disadvantages, for example, they are characterized by appreciable porosity, by only moderate tensile, compressive, and shearing strengths, and by poor chemical resistance toward certain chemicals, notably those of alkaline reaction. Furfuryl alcohol resins, on the other hand, in spite of their hardness, toughness, and chemical resistance, have not been manufactured commercially to any extent due to the difficulties encountered in controlling the initial condensation and final polymerization reactions and to the relatively high cost of the resinous product. In copending applications Serial No. 565,808 (now Patent No. 2,471,600, May 31, 1949) filed November 29, 1944 as a continuation-in-part of application Serial No. 511,600, filed November 24, 1943 (now abandoned), and Serial No. 547,971, filed August 3, 1944 (now Patent No. 2,416,038, February 18, 1947), processes for controlling the condensation of furfuryl alcohol and the polymerization of the initial resin are described and claimed, but, even with the availability of controllable processes, the uses of furfuryl alcohol resins may be limited by the cost thereof.

One object of the present invention is to provide hard, infusible, insoluble resinous compositions comprising a phenolic resin and a furfuryl alcohol resin, which compositions possess advantageous properties not to be expected from the known properties of either of the components thereof.

Another object of the invention is to provide hard, infusible, insoluble resinous compositions, the major component of which is a phenolic resin, and the minor component of which is a furfuryl alcohol resin, and which by reason of the furfuryl alcohol resin possess properties not heretofore available in the phenol-formaldehyde type of resin.

Still another object of the invention is to provide hard, infusible, insoluble resinous compositions, the major component of which is a furfuryl alcohol resin and the minor component of which is a phenolic resin, and which possess the desirable characteristics of a furfuryl alcohol resin but are less expensive than the furfuryl alcohol resins heretofore available due to the presence therein of the phenol-formaldehyde resin.

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A further object of the invention is to provide resinous compositions in the initial, convertible state of reaction which may be converted into the hard, infusible, insoluble resinous compositions referred to above.

Other objects, including the provision of novel methods for producing resinous compositions of the types states, will be apparent from a consideration of this specification and the claims.

In accordance with the present invention, a phenolic resin and a furfuryl alcohol resin are combined in the initial state of reaction to form a resinous composition which is convertible, for example by heat or acid or both, into a hard, infusible, insoluble resinous composition in its final state of reaction.

The term "a phenolic resin" includes the products so designated in the art by that term, namely, the reaction products of an aldehyde and a phenol capable of reacting therewith to form a heat-convertible resin. The phenol is advantageously a monohydric phenol such as phenol or a cresol or xylenol capable of reacting with an aldehyde to form a heat-convertible resin. The compound reacting with the phenol, referred to herein as a compound providing an aldehyde, may be a true aldehyde or a compound which under the conditions of reaction yields an aldehyde. Preferably, the compound providing the aldehyde, is a formaldehyde-supplying compound such as formaldehyde, paraformaldehyde, hexamethylenetetramine, or the like. The products obtained by reacting a formaldehyde-supplying compound and a monohydric phenol capable of reacting with the methylene-containing compound are included herein in the term "phenol-formaldehyde resin." In the preferred embodiment of the invention, the phenolic resin employed is obtained by reacting commercial phenol with formaldehyde. Mixtures of the various phenols or aldehydes may, of course, be employed. In view of this, the invention will be described using a phenol-formaldehyde resin as an example, but it is to be understood that other phenol-aldehyde resins may be used in place of the phenol-formaldehyde resin, if desired.

The phenol-formaldehyde resin may be obtaned by any suitable mehod, using either an acid or a basic catalyst, preferably the latter. The phenol-formaldehyde resin may be a one-stage resin, that is one which contains sufficient methylene-containing compound to be convertible

into the final state of cure, or it may be a two-stage resin, that is one to which an additional amount of methylene-containing compound must be added to obtain a convertible product. The phenol-formaldehyde resin will usually be of the type that is convertible by heat, but one of the phenol-formaldehyde resins which are convertible at room temperature in the presence of acid may be used if desired.

As is known, furfuryl alcohol will condense in the presence of acid to form a resinous composition, and the resinous composition employed in combination with the phenol-formaldehyde resin in accordance with the present invention may be formed by any suitable method. The furfuryl alcohol resin may be a one-stage resin, that is one that contains sufficient acid to be convertible into the final state of cure or it may be a two-stage resin, that is one to which acid must be added to obtain a convertible product. The acid added to the two-stage resin to render it heat-convertible may be a strong acid, in which case, the conversion may be brought about at room temperature, or the disclosure of our copending application Serial No. 511,600, filed November 24, 1943, may be followed and a latent acid catalyst added, in which case the resin is convertible by heat. As stated in that application, a latent acid catalyst is a compound which is neutral to slightly acid at room temperature and inactive to convert the resin during the working thereof but which is effective at least at an elevated temperature to liberate acid to cause polymerization of the resin to the infusible, insoluble stage. Reference may be made to that application for examples of such catalysts, an aromatic sulphonchloride, such as paratoluenesulphonchloride and an aliphatic amino salt of an aromatic sulphonic acid, such as ammonium paratoluenesulphonate being typical. If desired, for economic or other reasons, furfural may be included with the furfuryl alcohol in the production of the initial resin, but so far as the properties of the product are concerned, there is no advantage to be gained. If furfural is included, it may be present in amounts up to about 15% without deleteriously affecting the properties of the product. Advantageously, the initial condensation reaction of the furfuryl alcohol is controlled as described in one of the copending applications Serial No. 529,107, filed April 1, 1944 (now abandoned), or Serial No. 547,971, filed August 3, 1944 (now Patent No. 2,416,038, February 18, 1947), or Serial No. 556,657, filed September 30, 1944 (now abandoned).

The term "potentially reactive resinous composition" when used herein to designate the phenolic resin, the furfuryl alcohol resin, or the combined resin refers to the resin in its initial stage of reaction in which it is convertible to the final, hard, infusible stage. The term is applicable to both the one-stage and the two-stage resins, although in the latter case a methylene-containing compound or an acid or both must be added to the potentially reactive composition prior to its conversion to the final stage.

The initial phenol-formaldehyde and furfuryl alcohol resins may be combined in a number of ways. For example, the two resinous products may be prepared separately and then mixed together to form a homogeneous resinous product, or the two resinous compositions may be produced simultaneously, either by mixing the reactants together or by adding one or more of the reactants to a partially or completely reacted mixture of the other reactants. Both methods are included in the claims which recite the step of combining together potentially reactive phenolic resin and a potentially reactive furfuryl alcohol resin. In the case the two preformed resins are to be mixed, each composition is advantageously prepared in the form of a syrupy product and the two are then mixed together. Unless both of the resins are convertible to the final state of polymerization, the necessary acid and/or methylene-containing compound is added at the time of conversion of the product into the hard, infusible, insoluble product.

In the event the two resinous compositions are to be formed simultaneously, the furfuryl alcohol, the phenol, all or a portion of the methylene-containing compound, and an acid catalyst serving to produce both initial resins are mixed together and heated to cause reaction. In this case (a two-stage resin being formed) only about one-half of the formaldehyde required for heat-convertibility will be added, and the non-convertible resinous composition is then rendered convertible by adding the required amount of a methylene-containing compound to the initial reaction product.

As an example of the addition of one or more reactants to a partially or completely reacted mixture of the other reactants, the furfuryl alcohol may be first partially reacted using an acid catalyst and the phenol and formaldehyde may then be added together with sufficient alkali, such as sodium hydroxide, to neutralize the acid and leave an excess of alkali to serve as a catalyst for the reaction between the phenol and formaldehyde. The mixture after completion of the reaction may be distilled under vacuum following the usual procedure employed in producing phenol-formaldehyde resins. The initial product thus obtained may be hardened by the addition of an acid or latent acid catalyst for the furfuryl alcohol resin. Alternatively, the phenol and formaldehyde may be reacted first with a basic catalyst and the furfuryl alcohol may then be added together with sufficient acid to neutralize the basic catalyst and to catalyze the condensation of the furfuryl alcohol. After the completion of the reaction, the acid may be neutralized so that the furfuryl alcohol resin is a two-stage resin which requires the addition of acid or a latent catalyst to render it convertible.

As stated, the potentially reactive phenol-formaldehyde resin and the potentially reactive furfuryl alcohol resin may be one-stage or two-stage resins. A particularly desirable product is one containing a one-stage phenol-formaldehyde resin and a two stage furfuryl alcohol resin. A latent acid catalyst may advantageously be mixed with this combined resin prior to its conversion to the hard, infusible, insoluble stage.

The usual fillers, such as asbestos fibre, wood pulp, wood flour, mineral fillers, and the like, can be mixed with the initial resinous composition. For example, a filler such as asbestos may be added to the syrupy resin in a dough mixer and the mixture placed in molds in the product of "Haveg" products (see "The Chemistry of Synthetic Resins" by Carleton Ellis, Reinhold Publishing Corporation, 1935, pp. 458; 1332); or wood flour may be mixed with the initial resinous composition and the mixture compounded and compacted on rolls and ground to produce a molding powder. In addition, the composition may be dissolved in a solvent, such as acetone or a mixture of alcohol and benzol in equal parts, and the

solution used as a lacquer or to impregnate sheet material, such as paper or fabric, which may be dried, laminated, and subjected to heat and pressure between platens of a hydraulic press to form a laminated article.

The combination between the phenol-formaldehyde resin and the furfuryl alcohol resin involves more than a mere physical mixture of the two components. That this is so is demonstrated by a consideration of the viscosities and other physical properties of various combinations of the two resin components as shown in Figures 1 to 5 of the drawing and by the table of chemical resistance hereinafter discussed. In these charts and the table, the physical properties of a phenol-formaldehyde resin, a furfuryl alcohol resin, and various combinations thereof are set forth, A in Figures 1 to 5 representing the amount of phenol-formaldehyde resin present and B representing the amount of furfuryl alcohol resin present.

The phenol-formaldehyde resin was prepared as follows:

100 pounds of phenol, 80 pounds of 40% formaldehyde solution, and 5 pounds of concentrated ammonium hydroxide were refluxed gently together for about fifty minutes. The excess water was evaporated by vacuum distillation to about 60° C. under 30 inches of vacuum. The resin at the completion of the distillation contained about 25% total volatile, determined by baking the resin in a shallow dish for twenty-four hours at 150° C., and of this about 15% was water. The resin was a syrupy one-stage resin, that is, was convertible by heat into the final state of cure.

The furfuryl alcohol resin was prepared as follows:

To 100 pounds (10.6 gals.) furfuryl alcohol, there was added 13.6 pounds (1.59 gals.) of a solution of 50 grams/litre H_2SO_4, in a tank equipped for agitation. The temperature rose to about 50° C. in about ten minutes. At this point, 10 pounds (1.2 gals.) of water were added, which tended to reduce the speed of reaction. The temperature continued to rise and at 70° C., 90° C., and 100° C., 10 pounds (1.2 gals.) portions of water were added as before. The resin was allowed to react at 100° C. for about ten minutes to obtain the proper viscosity. When this point was reached, 50 pounds (6.0 gals.) of water was suddenly added to quench the reaction, followed by 0.6 pound of NaOH dissolved in 3.5 pounds of water. The resin was allowed to settle and the supernatant water was siphoned off. The non-reactive (two-stage) resin was then transferred to a still and was distilled under 26–29 inches of vacuum to a temperature of 125° C., thereby providing a substantially anhydrous resin. The resin so produced had a viscosity similar to that of molasses.

Referring first to Figure 1 showing the viscosities, these data were based on the resin in its initial state of reaction and were determined for the phenol-formaldehyde, and for the furfuryl alcohol resin described above and for the various mixtures thereof prepared by thoroughly mixing together the various percentages of these two resins. The method used for determination of the viscosities was the ball method which consists of timing the fall of a 10 mm. ball through a 6-inch column of resin held at 25° C. in a glass tube about 1¼ inches in diameter. It is to be noted from the figure that the phenol-formaldehyde resin and the furfuryl alcohol resin had viscosities of 56 and 60 seconds, respectively, and that all of the combinations of the two resins had viscosities higher than these, the maximum viscosity of 188 seconds occurring in a combination of 40% furfuryl alcohol resin and 60% phenol-formaldehyde resin. These viscosity changes, as well as the other physical advantages of combinations of the two resins, show that some unexpected phenomenon occurs when the two resins are combined. This may be a reaction of a chemical nature, possibly polymerization or intermolecular condensation, or a colloid chemical change, such as coagulation or aggregation of the molecules, but the invention is not to be limited by any possible explanation of the phenomenon.

Referring to the specimens for the tests set forth in Figures 2 to 5 and in the table, the phenol-formaldehyde and furfuryl alcohol resinous compositions and the resinous compositions containing the combined resins were made by mixing 5 pounds of the initial resin, or the desired amounts of the two initial resins required to equal 5 pounds, in a dough mixer or kneader to which was added 5 pounds of long-fibre asbestos. In the cases where the furfuryl alcohol resin was employed, 4% by weight of paratoluene sulphonchloride (a latent catalyst) based on the furfuryl alcohol resin was also added to the mixer. The contents of the mixer were mixed for fiteen minutes and the pasty compound was loaded into molds by tamping or rolling. The molds were shaped to produce the test specimens described hereinafter under the individual tests. The molded compositions were then baked for twelve hours under 100 pounds per square inch pressure at 290° F. After curing of the resin by this treatment, the specimens were removed from the mold and sanded.

In Figure 2, the tensile strengths of the various specimens are shown. The tensile strength was determined on a specimen ½ inch thick by 1 inch wide by 12 inches long with a "waist" reduced to ¾ inch wide. The samples were placed in a standard Olsen Universal testing machine and broken in the manner well known in the testing art. The tensile strengths of the compositions containing only one of the resins are not very far apart, the one containing only the furfuryl alcohol resin being slightly stronger. However, when one of the resins is combined with the other, the tensile strengths of the products increase until a peak of maximum tensile strength is reached in the combination containing about equal parts of the two resins. It is of interest to note that the curve for the tensile strengths of the products containing the combined resins is similar to the curve for viscosities.

In Figure 3, the compression strength of the two resins and of various combinations thereof are set forth. These figures were obtained on a 1 inch cube in an Olsen Universal testing machine in a manner well known in the testing art. The figure shows that the compressive strength of the product containing only the furfuryl alcohol resin is much higher than that of the one containing only the phenol-formaldehyde resin. Instead of changes in the compressive strengths following a straight line as the proportion of one of the resins is increased which would normally be expected, a much higher compressive strength is obtained at any given proportion than the proportional increase indicated by a straight line. Furthermore, the portion of the curve at the left is relatively flat, showing that considerable quan-

tities, up to 30% or 40%, of phenol-formaldehyde resin may be combined with the furfuryl alcohol resin without appreciably or seriously diminishing the compressive strength.

Figure 4 shows the shearing strengths of products containing each of the resins and of products containing combinations of the two, the shearing strengths having been determined on samples 1 inch wide by ½ inch thick by 6 inches long in an Olsen Universal testing machine in a manner known to those familiar with the testing art. As in the case of the compressive strengths, the resinous composition containing only the furfuryl alcohol resin has a much higher shearing strength than the one containing only the phenol-formaldehyde resin and those containing the combinations of the two resins possess greater shearing strengths than the proportional increase indicated by a straight line. In this case also, up to 30% to 40% and even 50% of phenol-formaldehyde resin may be combined with the furfuryl alcohol resin without materially reducing the shearing strength of the product.

In Figure 5, there is shown the porosity of the various products. The porosity was determined in each case by measuring the percentage of water absorbed by a sample of the product immersed in water for twenty-four hours at room temperature, after having been initially under vacuum for twenty-four hours with the water admitted while the specimen was still under vacuum. As shown by the figure, the porosity of the product containing only the phenol-formaldehyde resin is relatively high (about 4.7%) while that containing only the furfuryl alcohol resin is very low (about .2%). The decrease in porosity as the furfuryl alcohol resin is combined with the phenol-formaldehyde resin and the increase in porosity as the phenol-formaldehyde resin is combined with the furfuryl alcohol resin does not follow a straight line, but in the former a rapid decrease is obtained, while in the latter the curve slopes nearly horizontal for combinations of furfuryl alcohol with up to 30% to 40% and even 50% of the phenol-formaldehyde resin. Hence, substantial amounts of phenol-formaldehyde resin can be mixed with the furfuryl alcohol resin without seriously destroying the low porosity value of the furfuryl alcohol resin.

In the following table, the chemical resistance of the phenol-formaldehyde resin, the furfuryl alcohol resin, and combinations of the two resins are set forth:

TABLE

Chemical resistance

Sample	Phenol-Formaldehyde Resin	Percent Furfuryl Alcohol Resin	52 Hrs. 10% NaOH at 100° C.	740 Hrs. at 40° C. Pyridin
1	100	0	Destroyed	Destroyed.
2	90	10	do	Do.
3	80	20	Badly attacked	Bad cracks.
4	70	30	Attacked	Do.
5	60	40	Sl. attacked	Do.
6	50	50	Swollen	Cracks.
7	40	60	Sl. swollen	Fairly good.
8	30	70	Good	Good.
9	20	80	do	Do.
10	10	90	do	Do.
11	0	100	do	Do.

This table shows the resistance of various combinations of the phenol-formaldehyde and the furfuryl alcohol resins to two chemicals which seriously affect phenol-formaldehyde resins. It will be noted that as much as 30% or 40% phenol-formaldehyde resin can be added to the furfuryl alcohol resin without seriously lowering the chemical resistance of the resin toward these substances.

From the foregoing description of the charts and table and from the charts and table themselves, it will be clear, not only that the combination of the two resins involves some chemical or physical phenomenon but also that resins of various desired properties may be obtained by selecting the amount of one resin to be mixed with the other. In fact, when as small an amount as 1% to 5% of the furfuryl alcohol resin is mixed with the phenol-formaldehyde resin, an improvement in properties of the phenol-formaldehyde resin results and this improvement continues as the amount is increased. By the invention, therefore, the physical characteristics of phenol-formaldehyde resins may be improved. For an arbitrary definition, the combinations of resins containing up to 50% of the furfuryl alcohol resin with the remainder phenol-formaldehyde resin may be termed a phenol-formaldehyde resin with which is combined a furfuryl alcohol resin. In general in the production of such a resin, the amount of furfuryl alcohol resin will be at least about 5% and will generally be between about 25% and about 50% based on the total resin content. Likewise, those resins which contain up to 50% of the phenol-formaldehyde resin with the remainder furfuryl alcohol resin may be termed a furfuryl alcohol resin with which is combined a phenol-formaldehyde resin. With respect to these resins, it is to be noted that substantial amounts of the phenol-formaldehyde resin, for example 30% to 40% and even 50%, may be combined with the furfuryl alcohol resin without seriously affecting the desirable properties of the furfuryl alcohol resin with respect to compressive strength, shearing strength, porosity, and chemical resistance. By the invention, therefore, the cost of furfuryl alcohol resins may be reduced without detriment to the desirable properties of such resins. In general, when a furfuryl alcohol resin with which phenol-formaldehyde resin is combined is desired, the amount of phenol-formaldehyde resin will be at least about 5% and may be present in amounts up to about 50%, usually the amount present being between about 25% and about 40%, based on the total resin content. Furthermore, the addition of the phenol-formaldehyde to the furfuryl alcohol resin or of the furfuryl alcohol resin to the phenol-formaldehyde resin increases the tensile strength of the product, as shown in Figure 2.

The foregoing descriptions will serve as examples of the preparation of a phenol-formaldehyde resin, a furfuryl alcohol resin, and the mixing of the two preformed resins to provide a combined resin. The following example illustrates a method in which the components of one of the resins are added to a partially reacted mixture of the other resin:

100 grams phenol, 100 grams CH_2O, and 5 grams NH_4OH solution 28% were refluxed for thirty minutes and cooled. 100 grams furfuryl alcohol and 6 grams HCl solution 35% (enough to neutralize NH_4OH and leave an excess of acid) were then added. The mixture was warmed to 100° C. or until reaction became exothermic, and was maintained for fifteen minutes with cooling to control reaction. NaOH solution was then added to bring the pH of the mixture to 4–5; and the mixture was distilled under vacuum to 90° C.

Considerable modification is possible in the

methods of making and combining the phenolic resin and the furfuryl alcohol resin and in the proportions of the two in the combined resin without departing from the features of the invention.

I claim:

1. A potentially reactive resinous composition in the form of a viscous liquid which consists essentially of a potentially reactive, unmodified, syrupy, resinous product obtained by reacting phenol and formaldehyde and removing free water from said reaction product, and a potentially reactive unmodified, syrupy, resinous product obtained by acid-condensing a material selected from the group consisting of furfuryl alcohol and a mixture of furfuryl alcohol and not more than about 15% furfural and removing free water from said condensation product, the said phenol-formaldehyde resinous product being present in an amount between about 50% and about 25% based on the mixture of the said two resinous products.

2. A potentially reactive resinous composition in the form of a viscous liquid which consists essentially of a potentially reactive one-stage, unmodified, syrupy resinous product obtained by reacting phenol and formaldehyde and removing free water from said reaction product, and a potentially reactive two-stage, unmodified, syrupy resinous product obtained by acid-condensing a material selected from the group consisting of furfuryl alcohol and a mixture of furfuryl alcohol and not more than about 15% furfural and removing free water from said condensation product, the said phenol-formaldehyde resinous product being present in an amount between about 50% and about 25% based on the mixture of the said two resinous products.

3. The hard, infusible, insoluble resinous composition comprising the heat-converted product of the potentially reactive resinous composition of claim 1.

4. The hard, infusible, insoluble resinous composition comprising the heat-converted product of the potentially reactive resinous composition of claim 2.

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