

1

3,056,708

MINERAL FIBER MAT FORMATION

Frank J. Ball, Charleston, S.C., assignor to West Virginia Pulp and Paper Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed May 13, 1959, Ser. No. 812,828

11 Claims. (Cl. 154-44)

This invention relates to mineral mat formation and relates more particularly to the bonding in mat formation of mineral fibers such as glass wool, rock wool and slag wool produced by attenuation from the molten mineral.

The usual components of mineral fibers of the kinds above referred to are silica, lime, alumina, magnesia, soda, boric oxide and the like in different combinations, as well as small amounts of other ingredients. In the production of mineral mats the molten mineral is produced in the form of fibers or filaments by methods and apparatus well known in the art. Generally speaking, these methods involve the attenuation of the mineral mass while molten to fibrous condition, which is retained as soon as the molten mineral cools sufficiently to lose its flowable characteristics. In certain operations of this type the molten mineral is caused to flow through electrically heated sieve-like members in the form of tiny streams into a jet of steam or heated air. Alternatively, the molten mineral may be attenuated by mingling it with a blast of steam or air, the blast in such case accomplishing the attenuation of the mineral. Another known method of attenuation is to mingle molten mineral with a blast emerging from high temperature burners so that the mineral while carried by the blast from the high temperature burners becomes attenuated, the high temperature of the burners facilitating production of mineral fibers having especially small diameters. Attenuation of molten mineral may also be accomplished by centrifugal force utilizing a rapidly rotating spinning disc from which the attenuated filaments are flung into an atmosphere in which they cool to solid state.

Due to the fact that the mineral fibers are produced by attenuation from molten mineral, the fibers are formed under conditions of extremely high temperature both as regards the fibers themselves and the atmosphere in which the attenuation is caused to occur. While the fibers may be permitted to become formed into a mass, or into a mat-like body by causing fibers to become deposited by a felting action on a moving conveyor, it is desirable for many purposes, such as insulations for refrigerators, buildings or pipes and for filters, to strengthen the mat formation resulting from the felting of the fibers by the application of an adhesive bonding material for bonding the fibers together at their points of contact. The amount of binder employed may vary over a wide range, depending on the uses for which the bonded mineral fiber may be produced. Mineral fiber mats containing from about 1% to about 15% by weight of binder are widely used to provide thermal insulation. For such purposes mineral fiber mats are formed under conditions of little or no pressure so as to provide a low density material characterized by a multiplicity of interstices among and between the fibers. For products of greater density greater pressure may be applied during manufacture.

The binder employed for such fiber mats ordinarily is resin of the thermosetting phenol aldehyde type. In order that the fibers may be more effectively bonded, particularly when a low resin content is desired, mineral fiber mats have generally been produced by causing an aqueous solution of the phenol aldehyde resin in the "A" stage to be sprayed into the hot atmospheric medium for the attenuated mineral so that the fibers upon being caused to occur in mat formation carry the resin in adhesive condition. Upon initial attenuation of the mineral into fibrous form, the atmosphere immediately surrounding the fibers is at an extremely high temperature ap-

2

proaching that of the molten mineral, but as the fibers move from the zone of immediate formation both they and the atmosphere in which they occur in discrete form become progressively cooler, the fibers becoming felted in mat formation at a temperature favorable to curing the applied thermosetting resin so that as the formed mat is moved from the zone of its formation it may be immediately cured utilizing the residual heat from the fiber mat-forming operation. Overheating of the applied resin prior to curing is prevented or minimized by reason of the fact that the resin is introduced in an aqueous medium such as a dilute aqueous solution, the vaporization of the water from the sprayed droplets serving both to assist in cooling the atmosphere surrounding the fibers and to hold down the temperature of the droplets by reason of the heat of vaporization of the water content thereof that becomes converted to vapor. As the water content of the droplets is lost by vaporization, the droplets become more viscous and adhesive, and as the fibers approach curing temperature they become adherent thereto for bonding the fibers together at the points of contact in the felted mat formation in which they become deposited. The initial dilution of the resin with water may be varied according to the extent to which the fibers and the atmosphere surrounding them have become cooled at the time of the injection of the spray. In usual practice it is desirable to employ a relatively dilute solution of the resin such as a 10% solution so as to take advantage of the cooling effect of the vaporization of the water from the droplets of solution, and to introduce the solution spray at a point such that the sprayed droplets become converted to an adhesive viscous condition without overheating of the resin for bonding the felted fibers together at a temperature favorable for curing to thermoset condition. The resin solution, in any case, is sprayed into an atmosphere that is above the boiling point of water and may be at a much higher temperature approaching that of the molten metal at about 3000° F., the droplets being protected, as aforesaid, by their water content so as to prevent excessive thermal decomposition of the resin until the fibers and the atmosphere from which they become felted become cooled to a temperature of the order of 500° F. or less that is safe for the resin.

In a typical operation for the manufacture of glass fiber insulation an aqueous solution of an "A" stage resole of about 10% concentration is sprayed into an atmosphere of steam surrounding the hot attenuated glass fibers during their formation and deposition in mat formation, the resin becoming adherent in viscous adhesive condition to the fibers in the mat-forming zone at a temperature in the neighborhood of 450° F. so as to constitute about 3% by dry weight of the glass fiber mat that is formed. The glass fiber mat is formed on a continuous moving carrier to desired thickness and is immediately subjected to heat curing by passage through the curing oven in which the resin is held at about 450° F. for about five minutes. While the resin is still workable and adhesive the fiber mat formation may be subjected to pressure, the amount of pressure varying depending upon the density desired in the finished product. The application of pressure also may be resorted to in order that the mat may be of more uniform thickness, but application of pressure is optional and no pressure at all may be employed if desired. For thermal insulation the density of the mat may be of the order of 1.5 to 8 pounds per cubic foot, but by employment of greater pressure and heavier loading of the fiber with resin, e.g., up to about 60% or 70% by weight of the finished bonded mat, more dense products may be obtained.

One of the principal problems which heretofore has been regarded as a necessary incident of the formation

of bonded mineral fiber mats is that which is encountered by reason of the fact that the solution of "A" stage resole resin is sprayed into an atmosphere which, by reason of the nature of the operation, is so hot, while at the same time being continuously supplied and exhausted, that there is concomitant with the evolution of water vapor a relatively large percentage loss of the phenol aldehyde type resin due to its volatilization and loss into the atmosphere. Further losses occur during curing. Such losses frequently run as high as about one-third of the solids contained in the "A" stage resole that is employed even in the case of the resins commercially employed which are selected so as to hold down the resin losses as much as possible. Such losses are uneconomical and likewise constitute an undesirable nuisance because of the discharge of so much phenol aldehyde resin and resin components into the atmosphere. In addition to the foregoing, the losses of phenol aldehyde type binder likewise place a severe limitation on the type of binder which may be employed. Phenol aldehyde resins in the "A" stage become less volatile as the advancement of the polymerization progresses, but likewise become less soluble in water with the result that if attempt is made to reduce volatilization of the resin by advancement of the polymerization of the resin-forming components, the desired dilution for spray application cannot be obtained without the employment of an increased quantity of alkali to hold the resole in solution. However, such increased quantities of alkali are not regarded as permissible because of adverse action of the increased amount of alkali on the mineral and likewise because of its adverse effect on resistance to water and moisture. Phenol aldehyde "A" stage resoles prepared utilizing a relatively high molar ratio of formaldehyde to phenol for a given degree of advancement have a higher molecular weight than those prepared utilizing a lower molar ratio. For this reason phenol aldehyde resins have been commercially employed wherein the molar ratio of formaldehyde to phenol is in the neighborhood of 2.5:1 notwithstanding the fact that there are other resins wherein the molar ratio is lower which exhibit considerably greater strength on a weight for weight basis of retained resin, the reason being that for such other resins the losses become so excessive as to compel the employment of the resin that is less effective from the standpoint of strength.

It is an object of this invention to improve upon the production of mineral fiber mats of the character hereinabove referred to so as to greatly reduce the resin losses occasioned by volatilization of the resin into the hot atmosphere which accompanies the mineral fibers during their production and deposition in felted mat formation.

A further object of this invention is to provide a very substantial reduction in the cost of the resin content of bonded mineral fiber mats.

A further object of this invention is to provide substantially increased strength provided by a given weight of thermosetting resin contained in a mineral fiber mat.

According to this invention, the production of mineral fiber mats as hereinabove described has been greatly improved by the blending of lignin with the "A" stage resole that is sprayed into the hot atmosphere accompanying the attenuated mineral fibers so as to be present therein at least upon deposition of the fibers in felted mat formation, the lignin preferably being that which is or is chemically similar to that produced as a by-product of alkaline pulping using either the soda process wherein the pulping liquor contains sodium hydroxide or the sulfate process wherein the pulping liquor contains both sodium hydroxide and sodium sulfide. Such lignin is generally referred to in the art as "alkali lignin," this term likewise being used herein and in the claims.

The quantity of alkali lignin employed in the blend with the "A" stage phenol aldehyde resin may be very large in that very desirable properties have been ob-

tained using as much as nine parts of lignin to one part of "A" stage resole solids. On the other hand, the improvements afforded according to this invention are realized whenever a substantial amount of the alkali lignin is blended with the resole resin, although from a practical point of view it is desirable in any case to employ at least 0.1 part of lignin per part of resole resin solids. It is a significant and desirable feature of this invention that preferred properties may be obtained when the lignin constitutes from about 40% to about 80% by weight and optimum properties being afforded at about 60% to about 75% of the blend.

By utilizing this invention very great economies are made possible. Thus for a given amount of binder to be deposited on the mineral fibers the quantity of "A" stage resole which is lost by volatilization is very greatly reduced. The alkali lignin employed is substantially non-volatile and it likewise is the case that the combination of the resole resin with the lignin results in a substantial reduction in resole loss. The losses by volatilization, therefore, are reduced not only by reduction in the volatility of the resole carried in the hot atmosphere for deposit on the mineral fibers, but also by reason of the fact that a very large portion of the binder is provided by the non-volatile lignin component. The cumulative effect results in an extremely great curtailment in the loss of binder.

Further economies also result from the fact that alkali lignin is an extremely low cost by-product and from the fact that excellent properties are obtained when the lignin constitutes a major proportion of the blend with the much more costly synthetic phenol aldehyde resin.

It also constitutes an unexpected as well as valuable feature of this invention that the employment of alkali lignin results in greatly improved bonding strength as compared with the resin in the absence of the lignin. Thus by the use of alkali lignin strength increases of the order of 2 to 2.5 times have been obtained as compared with resins currently used for most effectively bonding mineral fibers. Such strength increases afforded by the binder enable products of greater strength to be obtained from a like amount of binder or, alternatively, enable products having the same strength characteristics to be produced using a lesser quantity of binder, thereby effecting further economies in addition to those previously mentioned.

Another feature and advantage of this invention resides in the fact that a wider selection of phenol-aldehyde resins is permitted due to the fact that the methylol groups through which self-polymerization of an "A" stage resole occurs likewise react with reactive groups of the lignin to form a product of co-resinification that is different from either the lignin or the product otherwise produced by the curing of the resin in the absence of the lignin. Thus it becomes advantageous rather than otherwise from the strength point of view to employ a resole prepared utilizing a high ratio of aldehyde to phenol, due to the fact that the greater percentage of methylol groups provides a greater number of groups reactive with lignin to create a high molecular weight resin product having a reduced volatility and whose molecular structure is favorable to high strength. Moreover, the presence of the higher proportion of methylol groups is favorable to reaction with relatively high proportions of lignin relatively to the resole and likewise tends to reduce volatility in the resole per se.

Lignin has had limited commercial utilization principally by reason of its physical and chemical characteristics. Thus lignin is not resistant to water and is soluble in alkaline solutions. Moreover, it is a non-thermosetting thermoplastic which tends to disintegrate if heated above about 200° C. and which, if formable at all from the amorphous powdered condition as recovered, merely provides a crumbly mass having little or no strength. It is for these reasons that the large quantities which occur as a by-product in the recovery of free cellulose fiber are

either sewered as it occurs in the solution separated from the fiber or is disposed of by partial evaporation of the water content of the lignin solution and spraying the resulting concentrate into a furnace wherein the lignin is burned and from which the inorganic treating chemicals used in the pulping operation may be at least partially recovered. When lignin is recovered from a pulping operation in dry condition, it generally is in the form of an amorphous brown powder and may be purchased from producers at a cost of only a few cents per pound.

Lignin as it occurs in natural ligno-cellulose material is a complex substance in the nature of a non-uniform polymeric structure in which the basic molecular configuration is believed to be derived from coniferyl-type alcohols with the creation of repeating propyl-phenol units. The exact structure of lignin, however, is uncertain. A vast amount of research work has been carried out to determine the structure of lignin, but to date no structure has yet been set forth which satisfactorily explains all the chemical and physical characteristics of lignin. The presence of ether linkages within the structure and the presence of benzene rings, methoxyl groups, and both alcoholic and phenolic hydroxyls have, however, been well established.

Lignin as it occurs in nature is generally termed "proto-lignin" and varies somewhat depending upon the particular source of the ligno-cellulose material. The principal variation in lignin, depending on its source, appears to be the number of methoxy groups present in the molecule. Thus it has been estimated that hardwood lignin contains about 20% to 21% by weight of methoxy groups, that lignin from soft woods contains about 14% to 15% by weight of methoxy groups, and that lignin from grasses contains only about 0 to 1% by weight of methoxy groups. However, the methoxy groups contained in lignin are substantially non-reactive and such differences in the content of methoxy groups are not regarded as having substantial importance in connection with the practice of the present invention.

When the proto-lignin content in naturally occurring ligno-cellulose material is separated from the cellulose fiber and later is recovered, the naturally occurring proto-lignin is affected by the recovery process, with the result that the lignin which ordinarily is referred to in the art is the lignin in its form as recovered, as distinguished from the proto-lignin occurring in the natural ligno-cellulose material. In the practice of this invention it is the recovered lignin which is employed and which is referred to herein. Due to the greater complexity of the naturally occurring proto-lignin it does not lend itself for use according to the present invention.

During pulping of natural ligno-cellulose material whereby the fibers are released from the natural ligno-cellulose the alkali lignin becomes dissolved in the pulping liquor as a salt of lignin, and is conventionally recovered from the pulping liquor by acid precipitation after the pulping liquor has been separated from the fibers. The alkali lignin can be recovered from such acid precipitation as free lignin or as a lignin salt, depending upon the specific conditions under which the lignin is obtained. If the lignin is precipitated at a high pH of the order of about 9.5 to 10.0, the salt of lignin is obtained. On the other hand, if the lignin is precipitated at a low pH of the order of about 2.0 to 5.0, or if the lignin precipitated at a high pH is acid washed so as to substantially free the lignin from its salt, free lignin is obtained. Moreover, lignin of slightly different characteristics can be obtained dependent upon the pH at which the lignin is precipitated from the pulping liquor. Thus a pulping liquor with a pH of 12.5 can be treated with acid to impart a pH of 10.0 whereby a fraction of the lignin content of the pulping liquor will be precipitated. But if the lignin thus precipitated is removed and the pulping liquor is further acidified to a pH of, say, 9.0, another fraction will be precipitated. This process can be continued until all the

lignin has been precipitated at a very low pH. The different fractions of lignin thus precipitated when in or converted to the free lignin form possess slightly different characteristics, such as solubilities due, it is believed, to lignin having slightly different molecular weights having been precipitated at the different pH levels.

In the practice of this invention it is distinctly preferable to employ alkali lignin in the free acid form which likewise is referred to herein as free lignin. However, when optimum conditions of combined strength and resistance to water absorption are of lesser importance lignin may be employed containing a substantial amount of inorganic material—typically lignin in its alkali metal salt form may be employed. However, it is normally undesirable to have an excessive amount of inorganic material in the binder for the mineral fiber and for this reason it normally is undesirable to employ lignin containing more than about 12% of ash. Moreover, the presence of substantial quantities of alkali metal is believed to have a deleterious effect on glass, particularly upon ageing, and for this reason as well as the reasons previously mentioned it constitutes preferred practice of this invention to employ free lignin, lignin containing less than 1.5% ash being regarded herein and in the claims as free lignin although lignin containing less than 1% ash provides still better practice of this invention. When reference is made herein to the employment of free lignin with a resole or in solution with a resole, it is to be understood that the reference is to the free lignin that is added or dissolved with the resole inasmuch as the ultimate disposition of the alkaline catalyst for the resole is a matter of considerable complexity.

As regards the combined resole and lignin, it is preferable in the practice of this invention that the blend of alkali lignin and resole contain not more than about 2% of ash and it is preferable that the ash be less than 1%. From the point of view of alkaline reactive metal, it is preferable that the alkaline reactive metal be not greater than 1% by weight of the solids in the cured resin. Lignin in the free acid form is insoluble in water, whereas lignin recovered so as to contain a substantial amount of alkali metal salt is water soluble. The term "alkali lignin" as used herein and in the claims has reference both to the soluble alkali metal salt form and to the water insoluble free lignin form.

When reference is made herein to "ash content," the reference is to ash content determined by placing 4 grams of resole or resole solution in a platinum crucible, heating at 135° C. for three hours and then heating in a muffle furnace at substantially 800° C. until constant weight is achieved, which usually requires about eight hours. Unless otherwise stated, the ash is expressed as percentage on the dry weight of solids.

The type of reactions between formaldehyde and a phenol by way of condensation and/or polymerization is substantially different depending upon whether these reactions are effected in the presence of an alkaline catalyst or in the presence of an acid catalyst. When an alkaline catalyst is employed, the initial reaction consists primarily in the production of methylol substituents on the benzene ring of the phenol and the reaction product initially produced is soluble in water or in certain organic solvents such as methanol or ethanol, with or without the presence of some water. The reaction product in this condition is referred to as "'A' stage resin" and such alkaline catalyzed products are generally referred to as "resoles." The "A" stage resole likewise is soluble in alkaline solutions and generally is initially used while in this stage. Further reaction results in polymerization of the methylol phenols to form a product that is insoluble in alkaline solutions, and the reaction product in this condition is commonly referred to as being in the "'B' stage." Further polymerization at elevated temperatures results in the conversion of the "B" stage resin into the thermoset condition in which it normally occurs

in manufactured products, this condition being generally referred to as the "C" stage." The different stages of reaction are effected without the addition of a curing agent. Alkaline catalysts commonly used for catalyzing phenol formaldehyde reaction are the oxides and hydroxides of alkaline earths and alkali metals, ammonia, and amines such as ethanolamine. The amount of catalyst may range from about 0.1% to 15%.

As distinguished from the resoles produced by alkaline catalyzed reaction between formaldehyde and a phenol, the presence of an acid catalyst results in a different reaction mechanism, resulting in more highly polymerized reaction products which are commonly referred to in the art as "novolaks." Such novolaks do not possess the solubility of the resoles, and are generally utilized by effecting a cure in the presence of a substantial quantity of a curing agent, such as hexamethylene tetramine.

It is essential in the practice of this invention that the phenol aldehyde be brought to the "A" stage prior to blending it with the lignin. In order that the phenol aldehyde be polymerizable by reaction with itself and reaction with the lignin, it is necessary that the reaction of the phenol and the aldehyde proceed until the reaction has resulted in the formation of the methylol groups which are characteristic of an "A" stage resole. If the lignin is blended prematurely with the phenol aldehyde the reaction to form the methylol groups which play an important part in the thermosetting reaction is interfered with.

"A" stage resoles are characterized by the substitution of one or more methylol groups at the reactive positions on the molecule of a phenol. In a typical resole as such the methylol groups react with hydrogens in active positions on other molecules of a phenol and, as hereinabove stated, when lignin is present the methylol groups on the phenol molecule are believed to react with the alcoholic hydroxyls of the lignin. A typical resole does not consist of a single compound but generally is a mixture of different isomers and homologs. Thus, according to Sprengling and Freeman, *Journal of the American Chemical Society*, vol. 72, pp. 1982-1985 (1950), the reaction product of formaldehyde with phenol at a ratio of one part phenol to 1.4 parts formaldehyde using sodium hydroxide as a catalyst results in the following composition.

Components of reaction product:	Mole percent present
Phenol	5-10
O-methylol phenol	10-15
P-methylol phenol	35-40
2,4-dimethylol phenol	30-35
2,4,6-trimethylol phenol	4-8

When the ratio of formaldehyde to phenol is greater than 1.4:1 the proportion of 2,4,6-trimethylol phenol (which also may be indicated as 2,4,2'-trimethylol phenol) is increased; and in the presence of a substantial amount of free lignin it is preferably that the resole contain a major proportion of trimethylol phenol.

The resoles that are commercially produced differ in the degree of advancement while still in the "A" stage depending on the uses for which the resoles are intended. In the foregoing tabulation of components found in a typical resole, the components are in essentially unreacted state prior to polymerization but actually in most commercial resoles a certain amount of polymerization has already taken place, depending on the degree of advancement short of conversion of the resole from the "A" stage to the "B" stage. The resole in the initial or low stage of advancement is water soluble and becomes increasingly less soluble as advancement progresses.

The production of an aqueous blend of lignin and "A" stage resole that is adapted to be sprayed is desirably accomplished by mixing an aqueous solution of "A" stage resole with an aqueous solution of lignin. For spray application the production of an aqueous solution con-

stitutes normal practice inasmuch as water is an inexpensive solvent and presents no recovery or safety problems. However, there is no technical reason why the solution may not comprise other solvent media such as ethanol or methanol inasmuch as the solvent medium is dissipated into the heated atmosphere in the initial fiber bonding step, wherein thermoplastic resin becomes deposited on the fibers. In the case of lignin in the form of its sodium salt, the lignin is freely soluble in water and the water solution of desired solids content may merely be commingled with an aqueous solution of "A" stage resole to provide an aqueous solution containing the desired solids content and the desired relative proportion of lignin and resole. In the case of free acid lignin, which is insoluble in water, an aqueous solution may be obtained by the employment of ammonia to convert the free acid lignin to its ammonium salt. About 4% of NH_3 based on the weight of the free lignin ordinarily is sufficient to effect complete solution. The solution may be readily effected by dispersing the lignin in powdered form in the desired amount of water and then admitting ammonia while agitating the slurry to effect intimate contact between the ammonia which becomes dissolved in the water and the lignin particles in suspension. The solution may be promoted by heat, e.g., to a temperature of about 180° F. The heat may conveniently be supplied by condensing steam in direct contact with the slurry. Instead of ammonia an amine such as dimethyl amine may be employed to solubilize the free lignin. Alternatively, an alkali metal oxide or hydroxide may be utilized to solubilize free lignin, but the employment of ammonia is preferred because it is volatile and does not introduce ash which results in degradation of moisture resistance properties.

In typical practice of this invention an ammoniacal aqueous mutual solution of free lignin and an "A" stage resole is prepared which contains from about 3% to about 50% of solids on the weight of the solution, e.g., about 10%, the ratio of resole to free lignin being such that there are about $\frac{1}{10}$ to 9 parts of lignin per part of "A" stage resole, e.g., about 3 parts to 1. For bonding a glass fiber mat wherein the glass fibers are produced by causing glass to pass through a multiplicity of minute orifices into high pressure steam with resultant solidification of the fibers while surrounded by the steam atmosphere, the aqueous ammoniacal solution is sprayed into the steam atmosphere in which the glass fibers are present prior to mat formation. The temperature under the conditions of high pressure steam introduction and heat supplied as the molten glass is introduced into the fiber-forming zone is considerably greater than the desired curing temperature, e.g., 450° F. The operation is ordinarily carried on so that the binder-carrying fibers when taken from the mat-forming zone will be at or close to the desired curing temperature. When the aqueous ammoniacal solution is introduced into the hot atmosphere both water vapor and ammonia are volatilized, with the result that the droplets which become intermingled with the discrete fibers become converted from the freely fluid condition as sprayed to a viscous adhesive condition wherein the lignin and the "A" stage resole are in mutual solution with each other in a heat plasticized condition. As the fibers become deposited in felted mat formation the adhesive droplets adhere to the fibers as a multiplicity of indiscriminately distributed particles so that as the fibers come in contact with each other the adhesive binder material causes the fibers to adhere to one another at their points of contact. The fibers are thus formed into a mat while carrying the binder as a continuous operation which permits the build-up of the mat to whatever thickness may be desired as the felted fibers are continuously carried, as by the means of a suitable carrier, from the area of initial deposit of the fibers in felted mat formation.

For insulation usages, the amount of binder resin car-

ried by the glass fiber may advantageously run from about 1% to about 15%, e.g., about 3%. While the added binder resin is still adhesive and heat plasticized, the mat may be compressed to whatever extent desired depending on the usage for which the bonded mat is intended. Satisfactory curing ordinarily is effected at temperatures between 250° F. and 500° F. maintained for about one minute to thirty minutes. Typically, the curing may be effected at about 450° F. for seven minutes.

When free lignin is employed in an ammoniacal mutual solution with the resole, the volatilization of the ammonia results in a lowering of the pH, and, while the resole employed is alkaline catalyzed, the acidity of the free lignin serves to lower the pH of the resole so that desirably the curing is effected under neutral or slightly acid conditions.

Inasmuch as the production of bonded felted mineral fiber mats involves the employment of large scale commercial equipment, a laboratory testing procedure is conventionally used as a screening test for determining the suitability of resinous binder materials. According to this laboratory test, the binder is applied to beads which are molded and cured in the form of a block having a dog bone shape which, after curing, is tested for its strength characteristics, the mineral of the beads being the same as that of the mineral fibers to be bonded. According to this test, the resinous binder to be tested is prepared in the form of an aqueous solution having a specified solids content such as 20% solids. Sufficient of the solution is added to the beads so that there will be a specified percentage of resin solids in relation to the weight of the beads. This percentage ordinarily is 3%. The beads carrying the resin solids are placed in a mold at about 450° F. to provide the dog bone-shaped testing piece and as soon as the mold is formed the molded beads are subjected to curing with externally applied pressure by holding at 450° F. for seven minutes. During the curing the volatile materials, such as water and ammonia, are expelled and the resin cures by thermosetting reaction. After the cured testing piece has been cooled to testing temperature, strength characteristics may be determined.

In obtaining the data referred to hereinbelow, the dog bone test blocks were produced using glass beads so as to have a cross-section at the neck of ¼ square inch. The test pieces were tested for tensile strength using a C. P. Universal Sand Strength Machine No. 401 manufactured by Harry W. Dietert Co., Detroit, Mich. The test employed was according to the Tentative Shell Tensile Test adopted by the American Foundrymen's Society, as published in the December 1955 issue of Modern Castings, except that glass beads were used instead of sand and except that the mold temperature was maintained substantially constant at 450° F. during both investment and curing instead of being cooled to 400° F. during investment followed by curing at 450° F. The glass beads employed had the following average sieve analysis.

Mesh:	Percent
140 -----	72.9
200 -----	17.7
325 -----	9.0
Pan -----	0.4

The very marked improvement in strength characteristics which is obtained by the blending of lignin with an "A" stage resole is clearly demonstrated in connection with the glass bead block test. "A" stage resoles prepared utilizing different molar ratios of phenol and formaldehyde in each instance were very decidedly benefitted by the blending of lignin therewith, as evidenced by very substantial increases in tensile strength.

In one series of tests an "A" stage resole was used which is of the type that has been commercially employed heretofore in the bonding of glass fiber mats. This resole,

which may be referred to herein for purposes of identification as Resole No. 1, is a resole prepared from phenol and formaldehyde in the ratio of about 2½ moles of formaldehyde to 1 mole of phenol. The resole is one which in preparation is alkaline catalyzed by the employment of barium hydroxide, the alkali before use of the resin being neutralized with sulfuric acid. This resole, which is water soluble, was mixed with a solution of free lignin utilizing about 2 moles of ammonia per 1 mole of lignin (taken as having an average molecular weight of 1,000) and the solution applied to the glass beads was prepared so as to contain 20% solids but with different ratios of lignin to resole. The solution was applied to the glass beads so that the resin solids constituted substantially 3% by dry weight of the cured block.

A similar series of tests was carried out in all respects the same as above described except for the substitution of another resole that is commercially used in the bonding of glass fiber mats, this resole being referred to herein as Resole No. 2.

Another like series of tests was carried out except that in this case the resole employed was trimethylol phenol. Trimethylol phenol is available commercially as an approximately 70% aqueous solution under the Bakelite Co., Inc. designation BRLA 1030. The viscosity at 25° C. of the BRLA 1030 which was used was 126 centipoises and its pH was 7.7, the ash content being 0.812% on a solids basis.

Another like series of tests was carried out except that the resole employed was a resole sold by Bakelite Co., Inc. under the trade designation BRL 1100. This is an "A" stage resole containing 67.7% solids, and having a viscosity of 105 centipoises at 25° C. and a pH of 7.7. The ash content of this resole is 0.384% on a solids basis. The product literature for this resole describes it as "A low viscosity phenolic resin which is infinitely dilutable with water for some time after manufacture. . . . BRL 1100 is used as a binder in the manufacture of glass wool insulating material and as an impregnant for densified wood."

The results of the foregoing series of tests utilizing Resole No. 1, Resole No. 2, trimethylol phenol and BRL 1100 are set forth in Table 1.

Table 1

Binder Blend		Tensile Strengths, p.s.i.			
Percent Lignin	Percent Resole	Resole No. 1	Resole No. 2	Trimethylol Phenol	BRL 1100
0	100	182	275	202	364
10	90	-----	358	328	402
20	80	-----	397	356	378
30	70	297	462	372	388
50	50	380	542	445	403
70	30	467	490	460	475
80	20	-----	505	478	443
90	10	293	267	258	285
100	0	42	42	42	42

It is noteworthy that whereas the lignin when used alone provides very low strength, much less as compared with that of the resole used per se, the addition of the lignin in each case resulted in a very substantial increase in strength even for only relatively small additions of lignin while further additions afforded strength increases as much as 2.5 times that imparted when employing the resole per se. It also is noteworthy that maximum strength is achieved when the lignin is in major proportion, the optimum being obtained when the ratio of lignin to resin is about 7:3, and that the strength is still high even when the ratio of lignin to resole is as much as about 9:1.

Additional tests were also made at a binder level of 1½%. Typical of the results of these tests were a strength of 200 p.s.i. obtained using a 70:30 lignin:Resole No. 1 mixture and a strength of 75 p.s.i. obtained using

straight Resole No. 1. It is interesting to note that at the 1½% binder level the lignin: resole mixture above gave a strength greater than the strength obtained using straight Resole No. 1 at a 3% level where twice as much binder was used.

Abraded glass particles of the cured test pieces using straight resoles when viewed under a stereoscopic microscope at a magnification of 90 showed marked differences from the glass particles where a lignin-resole mixture had been used. These differences may account for the great differences in strength which were obtained. Whereas the straight resole appeared to be primarily present on the glass beads in the form of small globules binding two or three beads together, the lignin-resole combination appeared to be evenly distributed on the glass beads in the form of a thin film. The distribution of the binder as a film, indicating greater flowability of the binder, permitted greater adhesion of the resin to the individual beads and also permitted the binding together of a much greater number of the beads.

The extent to which binder losses into a heated atmosphere are curtailed by the blending of lignin with an "A" stage resole resin is evidenced by a laboratory test, according to which a solution of binder to be tested is applied to a quantity of glass fibers in open mat formation so that the resulting coating as carried on the surface of the individual fibers are exposed to the atmosphere in which it is placed. The fibers are placed in a screen basket made from a medium weight copper wire window screening, the basket measuring about 2" x 2" x 2". The basket containing the glass fibers is dipped into an aqueous solution of the binder to be tested at a concentration of 20% solids, and the basket and the fibers are freed of excess binder solution by permitting the excess to drain from the basket. When the basket is drip-free it is immediately suspended in an oven at 450° F. The basket is weighed rapidly prior to being placed in the oven and at selected time intervals thereafter. The weighing is effected to the nearest .01 gram. During the residence of the sample in the oven there is loss of the aqueous solvent medium and, to the extent that the binder itself is volatile, there are losses of binder as well as the volatile solvent. Because the binder is applied by dipping, the binder solids relative to mineral fiber is higher than when the fiber is sprayed with binder solution in a usual commercial operation, and while the time within which substantially constant conditions are attained is higher for this reason, the test results obtained as to loss of binder correspond with those encountered in a commercial operation.

In Table 2 which follows the effectiveness of lignin in virtually completely preventing binder losses is demonstrated in contrast with the very large binder losses which occur in the case of conventional "A" stage resoles, the resoles subjected to this test being the Resole No. 1 and BRL 1100 hereinabove referred to when used alone, on the one hand, and, on the other hand, when used in combination with free lignin constituting 70% by dry weight of the binder blend:

Table 2

Time in Oven, Minutes	Grams of Binder Solution Retained			
	Resole #1, 100%	30% Resole #1, 70% Lignin	BRL 1100, 100%	30% BRL 1100, 70% Lignin
0.....	4.20	4.93	4.38	4.32
1.....	3.09	3.29	2.87	2.92
2.....	2.28	2.50	1.93	2.23
3.....	1.71	1.95	1.70	1.79
4.....	1.30	1.54	0.81	1.36
5.....	0.82	1.29	0.65	1.23
15.....	0.57	0.96	0.62	0.97
25.....	0.56	0.94	0.63	0.97
35.....	0.55	0.93	0.63	0.94
Applied Solids, gms.....	0.84	0.987	0.876	0.864
Percent Retained.....	65.5	94.2	71.9	109.3

It is apparent from the foregoing table that under the conditions of the test hereinabove described the loss of binder is of the order of about 28% to 34% in the case of the resins BRL 1100 and Resole No. 1, respectively.

When these resins were blended with lignin so that the lignin constituted 70% of the blend, then virtually complete recovery of the binder was effected. This is significant for it shows that in addition to the lignin being essentially non-volatile, the presence of the lignin likewise prevented virtually any loss of the resole. This is believed to be due not only to the physical effect of the lignin but also to the fact that at the oven temperature employed there is curing wherein the resole and lignin enter into a resinification reaction with the production of a resin having very low volatility as compared with the resole initially employed.

The use of lignin-resole binders in plant production of glass wool insulation has confirmed the results obtained in the laboratory tests. Using a lignin to resole ratio of only 1:2, glass wool insulation bats were made having very satisfactory properties. These bats when viewed under the stereoscopic microscope also showed the greater film-forming tendency as compared to the straight resole.

While it is preferable to produce an aqueous blend of lignin and an "A" stage resole by causing both the resole and the lignin to go into mutual solution, it is not necessary for either the resole or the lignin to be in true solution when sprayed into the hot atmosphere surrounding the mineral fibers. Thus while an alkali catalyzed resole may be diluted to the desired state of dilution without precipitation, one may employ an ammonia catalyzed resole of the type which tends to go out of solution upon dilution with water. In such case the resole may be diluted to form an aqueous dispersion of the resole and an aqueous solution of lignin may be added thereto. Such a dispersion may be sprayed into the hot atmosphere and upon exposure to the hot atmosphere, when the aqueous medium becomes volatilized, the dissolved lignin becomes deposited on the resole particles to form a solution therewith which is viscous and adhesive at the temperatures employed. Alternatively, a lignin dispersion may be mixed with a water soluble resole and in such case upon spraying into the hot atmosphere the resole becomes dissolved with the lignin so as to provide a viscous adhesive blend as the blend becomes deposited on the mineral fibers. For example, a lignin slurry may be prepared by carbonating a solution of free lignin in ammonia to precipitate the free lignin or, alternatively, the ammoniacal lignin solution could be precipitated with an acid such as hydrochloric acid. The resulting lignin precipitate either as a slurry or after filtering off excess water can be added to an aqueous solution of a water soluble "A" stage resole. Moreover, even if both the lignin and the resole are blended in the form of an aqueous dispersion the solids in the slurry as sprayed tend to coalesce with mutual solution of the lignin and the resole to provide the blend on the mineral fibers which may be heat cured by resin-forming reaction between the lignin and the resole. Any of the foregoing are comprehended by the term "aqueous liquid blend" of the lignin and resole, as this term is used herein and in the claims.

While the use of free acid sulfate pine lignin is highly effective, other lignin fractions and modified lignins may be advantageously utilized in the practice of this invention. Thus when free lignin was used which was prepared by precipitation of the lignin from the black liquor at a pH between 8 and 9.5, a tensile strength of 561 p.s.i., as determined by the above described glass bead bonding test, was obtained in the case of a blend containing 70% by weight of the free lignin and 30% of trimethylol phenol.

In the case of alkali lignin recovered from black liquor in the form of the sodium salt thereof rather than as free lignin, high tensile strength values likewise are obtained as the result of blending the lignin with an "A" stage

resole. Thus, utilizing alkali lignin recovered so as to contain about 9.2% ash, the tensile strength as determined by the glass bead bonding test was 488 p.s.i. in the case of a blend containing 70% by weight of the lignin and 30% of trimethylol phenol. However, the presence of the alkali metal in lignin is believed to have an adverse effect on mineral fiber when the lignin is comprised in the binder due to its attack on the mineral of the fiber upon ageing. It is for this reason in particular that the employment of free lignin is regarded as preferable in the practice of this invention. However, the alkali metal likewise has very serious adverse effect on water resistance.

Particularly high strength values have been obtained by the employment of free lignin which has been modified by reaction with formaldehyde. Using formaldehyde-modified lignin, a tensile strength of 527 p.s.i. was obtained as determined by the glass bead bonding test in the case of a blend of 70% by weight of the modified lignin and 30% trimethylol phenol. The formaldehyde-modified lignin was prepared by adding free lignin, formaldehyde and sodium hydroxide to water in the molar ratio of 1 mole lignin, 1.5 moles formaldehyde and 1 mole sodium hydroxide to form a 20% solution. The solution was heated to 190° F. for three hours to permit reaction and thereafter was diluted and acidified with sulfuric acid to a pH of approximately 2, the precipitated lignin formaldehyde product being recovered by filtration. The modified lignin was dissolved using about 10 moles of ammonia per mole of lignin and the resulting solution was mixed with trimethylol phenol to obtain the 20% binder solution applied to the glass beads.

In addition to the foregoing, it is possible to otherwise modify the alkali lignin that is used in the practice of this invention. Thus, as hereinabove stated, the methoxy group content of the lignin is relatively inert, and this being the case, the methoxy radical content of the lignin may be wholly or partially removed from the lignin molecule with complete or partial replacement of correspondingly positioned hydroxyls. Lignin may also be modified by reaction to form either an ester or an ether so long as such treatment does not exhaust the reactive groups of the lignin molecule. To the extent that such non-reactive radicals are added, the reactivity of the lignin with the resole or resole components becomes diminished and while lignins thus modified may be used, their use ordinarily is less desirable except in so far as the resulting modification of the viscosity characteristics of the lignin may have utility for special purposes.

While in normal practice of this invention the binder consists substantially entirely of a blend of "A" stage resole and alkali lignin, the practice of this invention admits of the presence of other substances such as conventional plasticizers. As much as about 35% by dry weight of the binder blend may be comprised of other substances, but preferably any such other substances constitute less than 10% by dry weight of the binder blend. A blend consisting of 35% by weight of free lignin, 30% of trimethylol phenol and 35% of furfuryl alcohol when subjected to the glass bead bonding test gave a tensile strength of 332 p.s.i. When the proportions were changed to 65.4% of free lignin, 28.06% of trimethylol phenol and 6.54% of furfuryl alcohol the tensile strength was 522 p.s.i. In another glass bead bonding test an ammonium soap of rosin acid was employed and a tensile strength of 415 p.s.i. was obtained in the case of a binder blend containing 35% by weight of free lignin, 30% of trimethylol phenol and 35% of the ammonium soap of rosin acid.

While this invention ordinarily is practiced in connection with conventional phenol-aldehyde resoles produced by reaction between phenol and formaldehyde in an aqueous medium in the presence of an alkaline catalyst, the resole need not necessarily be prepared from phenol and formaldehyde. Thus, in addition to phenol,

other substances in the class of phenols may be used such as cresoles, xylenoles, para-tertiary butyl phenol, para-phenyl phenol, bis-phenols, and resorcinol and when reference is made to the employment of a phenol the reference includes such compounds. In addition to formaldehyde, other aldehydes may be used such as chloral and benzaldehyde. More generally, any phenol or aldehyde may be employed which is reactive in the presence of an alkaline catalyst to produce an "A" stage resole and adapted to be further cured through the "B" and "C" stages, as these terms are commonly used in the art. As has been described more fully hereinabove, such resoles are characterized by the substitution of one or more methylol groups at the reactive positions on the molecule of a phenol.

While this invention has been described in connection with various examples and specific ways of practicing this invention, it is to be understood that this has been done for purposes of illustration and that the practice of this invention may be varied within the scope of the principles employed in the practice thereof as hereinabove set forth.

I claim:

1. In the production of a mat of mineral fibers by attenuation from molten mineral and the application of a binder thereto for bonding the fibers together upon becoming felted into contacting mat formation by spraying said binder in an aqueous liquid medium into an atmosphere that is heated to a temperature above about 212° F. and into contact with said attenuated fibers for effecting a bond between said fibers where they come into contact in said felted mat formation, the improvement which comprises spraying into said atmosphere droplets of an aqueous liquid blend of an "A" stage resole with from 0.1 to 9 parts by dry weight of lignin per part of said resole, said droplets in said heated atmosphere becoming converted by loss of water vapor therefrom to a viscous adhesive blend of said resole and said lignin that adheres to said fibers upon deposit thereon and bonds said fibers together where said fibers carrying said adhesive blend are in contacting relation, and thereafter heat curing said adhesive blend in situ as carried by said fibers to effect a resin forming reaction between said resole and said lignin.

2. In the production of a mat of mineral fibers by attenuation from molten mineral wherein the molten mineral is attenuated in the form of fibers into a moving body of heated atmosphere from which the fibers are felted into mat formation, a binder being applied to said fibers for binding them together by spraying said binder in an aqueous liquid medium into said moving body of atmosphere and into contact with said fibers for effecting a bond between said fibers where they come into contact in said felted mat formation, the improvement which comprises spraying into said heated atmosphere droplets of an aqueous liquid blend of an "A" stage resole with from 0.1 to 9 parts by dry weight of alkali lignin per part of said resole with evaporation of water vapor from said droplets and deposition of said droplets on said fibers in the form of a multiplicity of binder particles that bond said fibers together upon said fibers becoming felted into said mat formation, said fibers becoming cooled as felted in said mat formation to a temperature between about 250° F. and 500° F. at which said binder particles are cured in situ.

3. A method according to claim 2 wherein said fibers are glass fibers which are attenuated into a moving body of steam-containing atmosphere and said droplets are sprayed into said steam-containing atmosphere.

4. In the production of a mat of mineral fibers by attenuation from molten mineral and the application of a binder thereto for bonding the fibers together upon becoming felted into contacting mat formation by spraying an aqueous solution of said binder into an atmosphere that is heated to a temperature above about 450° F. and into contact with said attenuated fibers for effecting

15

a bond between said fibers where they come into contact in said felted mat formation, the improvement which comprises spraying into said atmosphere an aqueous mutual solution of an "A" stage resole and alkali lignin, the dry weight ratio of lignin to resole being from about 1:9 to 9:1 and the solids content of said solution being from about 3% to about 50%, and said droplets losing water therefrom by evaporation for deposition on and among said fibers in the form of a multiplicity of adhesive binder particles the solids content of which constitutes from about 1% to about 15% by weight of said mineral fibers, and thereafter heat curing said binder particles to effect a resin forming reaction between said lignin and said resole.

5. In the production of a mat of mineral fibers by attenuation from molten mineral and the application of a binder thereto for bonding the fibers together upon becoming felted into contacting mat formation by spraying said binder in an aqueous liquid medium into an atmosphere that is heated to a temperature above about 212° F. and into contact with said attenuated fibers for effecting a bond between said fibers where they come into contact in said felted mat formation, the improvement which comprises spraying into said atmosphere droplets of an aqueous ammoniacal mutual solution of free lignin and an "A" stage resole, there being from about 0.1 to 9 parts by dry weight of said lignin per part of resole and said droplets in said heated atmosphere becoming converted by loss of water vapor therefrom from fluid condition to a viscous blend of said resole and said lignin that adheres to said fibers upon deposit thereon and bonds said fibers together where said fibers carrying said adhesive blend are in contacting relation, and thereafter heat curing said adhesive blend in situ as carried by said fibers to effect a resin forming reaction between said resole and said lignin.

6. A method according to claim 5 wherein the solids content of said aqueous ammoniacal solution is from

16

about 3% to about 50% by weight and when cured in situ as deposited on said fibers constitutes from about 1% to about 15% by weight of said mat.

7. A felted mineral fiber mat containing a multiplicity of indiscriminately distributed particles of a thermoset resin binder which bonds said fibers together at points of contact between said fibers and which is the product of heat curing a blend of an "A" stage resole with from 0.1 to 9 parts by weight of alkali lignin per part of said resole.

8. A felted mineral fiber mat according to claim 7 wherein said particles constitute from about 1% to about 15% by weight of said mat and the density of said mat is between about 1.5 and about 8 pounds per cubic foot.

9. A felted mineral fiber mat according to claim 7 wherein the lignin is a major proportion of the blend.

10. A felted mineral fiber mat according to claim 7 wherein said alkali lignin is free lignin.

11. A felted mineral fiber mat according to claim 7 wherein said lignin is free lignin modified by substantial reaction with formaldehyde.

References Cited in the file of this patent

UNITED STATES PATENTS

2,161,749	Samaras	June 6, 1939
2,317,487	Schuelke	Apr. 27, 1943
2,338,839	Cross	Jan. 11, 1944
2,550,465	Gorski	Apr. 24, 1951
2,604,427	Armstrong	July 22, 1952
2,683,706	Muller	July 13, 1954
2,697,056	Schwartz	Dec. 14, 1954
2,830,648	Haddox	Apr. 15, 1958

OTHER REFERENCES

Publication, Industrial Uses of Alkali Lignin, by E. B. Brookland, Paper Trade Journal, vol. 122, No. 13, pages 138, 139 and 140, March 28, 1946.