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FRICTION MATERIAL AND METHOD OF MAKING SAME

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This invention relates to improvements in the production of friction material suitable for use as brake linings, clutch facings and the like.

The invention further relates to the production of a phenol-aldehyde condensation product of specific character and to the combination thereof as the principal binder component in and in the production of materials of the foregoing character.

The invention is particularly concerned with improvements in the production of friction material, such as brake linings, by extrusion of a friction material composition in continuous strip form, either with or without a reinforcing backing, followed by heat-curing of its binder content. It will be understood that the term "extrusion" is intended to include such methods as the forcing of a friction material mix under pressure, such as by means of a feed screw, through a die or shaped orifice, and rolling or calendering of a like mix by feeding it by gravity between a pair of conventional extrusion rolls of the class wherein one roll, having a knurled periphery, projects into a U-shaped periphery of another roll providing a laterally confined opening between the rolls.

In the formation of friction material mixes for such extrusion, a mixture is made, in a suitable device, such as a dough mixer, of short fiber asbestos, conventional friction material fillers, and binder including binder solvent, such solvent being sufficient to permit good distribution of the binder over the mix, but limited in amount so that the mix may be reduced to the form of relatively dry but somewhat tacky granular particles which can, however, be fed by gravity to the described extrusion rolls where the particles are compacted and shaped into continuous strip form. Mixes for extrusion must not be too wet or too tacky, nor composed of large lumps of very soft stock since, in such condition, they cannot be properly compacted and shaped, i. e. extruded, because of slippage, and further use of excessive or high solvent proportion results in much shrinkage and subsequent distortion of the friction material when cured.

It has heretofore been conventional to employ drying oils or resin-modified oils alone or together with rubber as binder for said compositions, together with adequate amounts of hydrocarbon solvents to dissolve the rubber and to adequately extend the oil so as to enable proper spreading and uniform distribution of the binder throughout the mix. The curing of material shaped from such mixes required prolonged and careful heat

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control for the purpose of hardening of the oil by polymerization and oxidation and for volatilizing the solvent. In addition to the many hours required for such curing, difficulties in handling and character of final product are often encountered by reason of rate and non-uniformity of binder cure, premature surface drying of the oil or "case hardening" resulting in solvent entrapment and the like. Further, the employment of oil in the initial mix is not entirely satisfactory as a sole binder for providing adequate tack and strength desirable in the production of a non-reinforced green strip material by the extrusion process.

In accord with the present invention, I eliminate the employment of drying oils and modified drying oils as a binder component in the production of friction materials of the aforesaid character, general composition and method of manufacture, by employing as the sole or principal binder component, an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin product of specific character. That is to say, these phenol-aldehyde solutions which I have found suitable are aqueous alkaline solutions, resulting from condensation in the presence of a caustic alkali catalyst, they have a characterizing high solids content range, and are further characterized by the degree of the initial condensation reaction as evidenced by their dilution factor, that is the amount of water that can be added before precipitation occurs, as will be hereinafter more fully set forth.

The employment of conventional phenol-aldehyde resins in alcohol or acetone solvents in the foregoing process has not been found satisfactory because such solutions are too tacky to be handled and extruded in the manners described, and further these solvents evaporate too readily, forming hard nodules and leaving no plasticity necessary for the extruding operation.

Conventional aqueous emulsions of such resins are likewise unsatisfactory since these emulsions readily break due to acidity of various materials in the friction composition mix which tend to neutralize emulsifying agents such as soaps employed, causing precipitation of the resin in an extremely viscous condition which is worse than when employing alcohol solvent, since there is no solvent when the water separates, and all that could possibly be done would be to add alcohol solvent, which then would have the same deficiency as the alcohol soluble resins. If emulsions do not "break," then there is no tackiness whatsoever necessary for extrusion.

The oil-modified phenolic resins are likewise unsatisfactory. Although they may be handled in hydrocarbon solvent and can form satisfactory mixes and be extruded, they are not readily thermosetting and do not cure to the same degree as ordinary phenolic resins. This results in loss of stability of the friction material, fading and distortion under the influence of brake generated heat in use, causing uneven wear and shortened life.

As distinguished from the foregoing, my aqueous resin solutions while originally viscous are not tacky and permit good mixing and distribution throughout the asbestos and other friction material components, and after some lapse of time adequate for good mixing, say about one-half hour, some of the water evaporates and the resin solution develops a limited but desirable tacky character, but this degree of evaporation is not as rapid as when employing alcohol or acetone solvents. Thus, for example, my new mix can stand for two or three days without becoming too dry and hard. Even so, if it should become too dry, it can be reconditioned by adding back a little water. This is not feasible with the alcohol soluble resins because the solvent dries too rapidly, even during the attempt to disperse the alcohol, and even so such resins are not quickly responsive to such treatment after they have dried in the mix. As distinguished from them, my water-soluble resins do not dry as hard when some of the water evaporates.

The aqueous resin solutions which characterize my invention have a solids content of from about 50% to about 80% by weight. Below about 45%, their employment results in mixes too wet to handle in that pastes are formed which do not extrude properly, and to remove excess water from the mix would require prolonged aging or heat drying, resulting in undesirable advancement of the resin and partial curing. Above about 80% solids, it is too viscous, dries too rapidly and does not have enough volume to cover the mix.

My aqueous resin solutions are further characterized by the degree of the resin condensation reaction, as determined by their "dilution factor," or extent to which their solutions may be diluted with added water before the resin precipitates. That is to say, although my partial condensation products are water-soluble, they are not infinitely dilutable but rather are of limited degree of dilutability. If they were of infinite dilutability, they would not be productive of desired tack in the mix. Thus, the resin solutions which are useful in accordance with the present invention have a dilutability or solubility in water of 1 part resin solution to 3–8 parts water as referred to a 50% solids aqueous solution, although I prefer to operate in the "dilution factor" range of 1 to 3–6. Thus, although I may employ resin solutions of different solids content, within said range, to suit the particular friction formulation employed, and resin solutions reacted or condensed to different degrees so that each particular resin solution can tolerate its own specific amount of dilution water before precipitation occurs, their useful range lies between tolerance of from about 3 to about 8 parts of dilution water before precipitation occurs as referred to a 50% solids solution.

In carrying out the resin condensation reaction, the reagents are employed in as concentrated a condition as possible resulting normally in a solution of about 50% solids content. If below this, or if it is desired to produce a solution of higher solids content range, excess water present may be removed by mild heating under vacuum so as to inhibit or prevent undesired advancement of the reaction, and this may best be effected at an intermediate point and determined by the dilutability test while carrying out the condensation reaction.

If desired, although unnecessary and impractical, the condensation reaction may be prematurely terminated at a point for example where a 50% solids solution has a dilution factor of 10 parts water to 1 part of such solution. This dilution factor may change on aging, i. e. by standing for several months, and go down to a dilution factor of 6 to 1 and thus within the useful range. On the other hand, a solution formed at a 2 to 1 useful dilution factor, may on standing become reduced to say a dilution ratio of ½ to 1 and become useless.

I may employ as the phenol reactant, phenol, cresols, cresylic acid, xylenols, resorcinols, or their mixtures. As the aldehyde reactant I may employ formaldehyde, paraformaldehyde, or other polymers of formaldehyde which react as formaldehyde. As the caustic alkali I may employ sodium or potassium hydroxide. The amount of alkali catalyst will vary with the reactant and desired rate of reaction. The aldehyde is employed in slight excess, such as for example about 2½ mols thereof to 2 mols of the phenol. The caustic alkali is preferably employed in an aqueous solution of between 30–40% concentration. The rate of reaction will also vary with the reactants, their concentration, and the time required, if any, for removal of water to bring the reaction mixture to the desired solids content.

Thus, for the purpose of illustration, I may employ reactants in the following amounts: 318.5 pounds of 90% synthetic phenol, 300 pounds of 41% formaldehyde and a 40% caustic soda solution made of 2700 grams of sodium hydroxide dissolved in water to make 7125 cc. This is equivalent to 100 parts by weight of phenol, 41 parts of formaldehyde and 2.00 parts of sodium hydroxide.

The reaction is carried out by controlled heating under reflux condensation. The phenol and formaldehyde are first added to the reaction vessel and heated to about 150° F., after which the caustic soda solution is added at intervals in about 5 equal parts over a period of about one hour. The temperature gradually rises to 210° F. at which point boiling and refluxing commences. Here test may be made to determine degree of condensation by the aforementioned dilutability or volumes of water required to cause precipitation. If the dilution factor and solids per cent are within the foregoing prescribed limits, heating is stopped and the product cooled. If the solids content is too low, water may be removed under vacuum distillation at a reduced temperature to prevent undue advancement of the resin condensation reaction, such as, for example, by employing a vacuum of 20 to 26 inches mercury permitting boiling at 120°–140° F. If at this point the reaction has not been carried to the desired point, careful and further mild heating, such as at a temperature of about 145°–155° F., after termination of vacuum distillation, may be employed with intermittent sampling. The total time of the reaction process may require from about one hour to about two hours, depending on the extent to which it is desired to carry the condensation reaction and

additional time may be required for removal of undesired water.

In a similar manner a partial condensation resin reaction product may be prepared by employing 200 grams of commercial cresylic acid, 216 grams of 37% formaldehyde, and 12 grams of caustic soda made up to 24 grams with water. This is equivalent to 1 mol cresylic acid to about 1.4 mols of formaldehyde, and 6% sodium hydroxide based on the cresylic acid. The foregoing mixture, reacted as in the preceding example, gave a solution of 55% solids content having a dilution ratio of 4½ to 1.

The following is an example of the formation and production of brake lining in continuous strip form by the roll extrusion method wherein my resin solution acts as the sole binder: 29.7 parts by weight of a 53.3% solids aqueous solution of my alkali catalyzed resin having a dilution ratio of 3½ to 1, was mixed with 42.2 parts by weight of short asbestos fiber and 28.1 parts by weight of conventional friction material fillers, including lubricants, friction augmenting agents and resin cure accelerator. The materials were mixed in a dough mixer until the resin solution was evenly distributed and the mix had a comminuted texture and was in the form of a loose mass of small pellets or nodules. This is permitted to age at room temperature for one or two days and then pulverized in a hammer mill to produce relatively uniform particles, which are generally termed "granules" of irregular shape and roughly of $\frac{1}{16}$" to $\frac{1}{8}$" in diameter. This mass is loose, flows by gravity, is highly compressible and the particles while normally dry have strong tack on being pressed together. These granules may then be compacted into strip form by feeding them by gravity between the rolls of the previously described roll extruder, and although the resultant strip material has good green strength, I may suitably combine therewith a wire mesh reinforcing backing by passing a wire strip through the rolls simultaneously with the feed stock. The strip material may be cut into desired lengths and the water content first evaporated, and thereafter the resin fully cured by heating in an oven at a temperature of about 400° F. for about 1–3 hours. As distinguished from this, similar friction material formed with a drying oil containing binder might, after removal of solvent, require heating for an elapsed time of about 30 hours for binder cure.

Although I have shown in the foregoing example the production of friction material wherein the resin solution is the sole binder, I may in the alternative replace a minor portion thereof or supplement it by a minor portion of other conventional friction material binder, such as, for example, natural or synthetic rubber, in either normal or peptized condition, together with requisite hydrocarbon solvent therefor.

I claim as my invention:

1. A friction material composition adapted to be compacted and shaped under pressure, comprising fibrous asbestos, fillers, and as the principal binder therefor, an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution.

2. A friction material composition adapted to be compacted and shaped under pressure, comprising fibrous asbestos, fillers, and as the principal binder therefor, an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 6 parts water as referred to a 50% solids solution.

3. An extrudable friction material composition composed of granules of an intimate admixture of short fibrous asbestos, fillers, and as the principal binder thereof, an aqueous caustic alkali solution of a thermosetting partial condensation resin alkali catalyzed reaction product of phenol and a molar excess of formaldehyde, said solution having a solids content of from about 50% to about 80% by weight, the resin being characterized by a limited dilutability before precipitation thereof from solution of 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution.

4. An extrudable friction material composition comprising an intimate admixture of short fibrous asbestos, fillers, and as its sole binder an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution.

5. The method of making friction material, which comprises intimately admixing with a short-fiber asbestos friction material composition, and as the principal binder therefor an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution, reducing the mix to a mass of non-coherent granules, and compacting and shaping the material into continuous strip form.

6. The method of making friction material, which comprises intimately admixing with a short-fiber asbestos friction material composition, and as the principal binder therefor an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 6 parts water as referred to a 50% solids solution, reducing the mix to a mass of non-coherent granules, and compacting and shaping the material into continuous strip form.

7. The method of making friction material, which comprises intimately admixing with a short-fiber asbestos friction material composition, and as the principal binder therefor an aqueous solution of a thermosetting partial condensation resin reaction product of phenol and formaldehyde haivng a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution, comminuting and tempering the mix to a flowable granular condition, compacting and shaping

said granules into continuous strip form and curing the binder.

8. The method of making friction material, which comprises intimately admixing with a short-fiber asbestos friction material composition a binder composed of an aqueous solution of a thermosetting partial condensation phenol-aldehyde resin reaction product having a solids content of from about 50% to about 80% by weight, the resin having a limited water solubility, said solubility being 1 part resin solution to from 3 to about 8 parts water as referred to a 50% solids solution, reducing said mixture to a loose, flowable, granular condition, calendering the

material into dense, strip form, and curing the binder thereof.

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