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BONDED FIBROUS SHAPE AND METHOD OF MAKING SAME

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5 Claims. (Cl. 260—19)

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This invention relates to products having properties adapting them for use as friction brake linings and packings. The invention is particularly directed to the manufacture of molded shapes or fabric sheets containing asbestos or other mineral fibers and also containing as a binder and filler tough and heat stable organic materials adapted to impart strength and wear resistance to the product.

In the manufacture of friction linings for automotive brake shoes, it has been common practice to improve the strength of felted or woven asbestos fiber fabrics or molded shapes by incorporating therein as binders or impregnants polymerizable fatty oils or oil modified resins which, upon solidification by heat treatment, develop hard stiffening bonds coating the fibers, or filling interstices between the fibers. Such compositions have exhibited an undesirable tendency to deteriorate with age and to lose resilience and strength, while becoming brittle and developing cracks. The polymerized fatty acid or fatty oil modified binders and impregnants also deteriorate rapidly when exposed to high temperatures, by loss of normal toughness and strength. Under conditions of severe braking service, brake linings incorporating such polymers exhibit serious loss of tensile strength and resistance to wear.

The polymerization of unsaturated fatty acids, fatty oils and fatty oil modified resins is usually accompanied by some oxidation. This oxidation takes place at the ethylenic linkages or other unsaturated points within the fatty acid molecule. The deterioration in heat stability, toughness and strength which generally accompanies polymerization hardening of fatty oils probably results primarily from excessive oxidation of the fatty acid or fatty ester molecule. Excessive oxidation carries the hardening reaction beyond the point necessary to form tough and heat stable bonds. In other words, excessive oxidation develops brittleness and cracking.

A primary object of the present invention is to provide tough and wear resistant sheets and shapes having a high degree of heat stability and resistance to deterioration.

Another object is to provide a simple and economical method of manufacturing sheets and shapes having properties particularly adapting them for use as brake linings and the like.

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A feature of the compositions of the present invention resides in their inherent resistance to deterioration or excessive oxidation, and in their capacity to retain after polymerization hardening, a high degree of resilience, cohesive strength and good wear and friction characteristics, throughout a long life and under exposure to a wide range of temperatures, including the high temperatures encountered in severe braking service. Another advantageous feature of the present compositions is their resistance to oils, moisture and chemicals.

With the above objects and features in view, the invention consists in the improved heat and wear resistant sheets and shapes and the method of manufacturing the same, which are hereinafter described and more particularly defined by the accompanying claims.

The tough and heat stable sheets and shapes which are manufactured in accordance with the present invention incorporate as their principal ingredients fibers of the type of mineral wool and asbestos, together with polymerized resorcinol-coupled fatty acids or fatty oils as binders or fillers. The binder or filler constituent of the fiber-binder compositions of the invention comprise polymers of modified unsaturated fatty acids or fatty oils of the type of linoleic acid or linseed oil, in which the fatty acid molecule has been modified prior to polymerization by coupling thereto one or more resorcinol molecules. The fatty acid molecule as thus modified by coupling resorcinol thereto, develops on heat polymerization a tough and heat stable product which is resilient and wear resistant and which exhibits substantially no tendency to deterioration by oxidation or otherwise, during normal aging periods or under severe conditions of wear and high temperature service.

The resorcinol-coupled fatty acid polymers have excellent adhesive properties and exhibit a high degree of affinity for inorganic fibers and fillers. For compounding brake lining such resorcinol-coupled fatty acid polymers may be employed both as binders and as wear and friction resistant fillers. Also, the resorcinol-coupled fatty acid polymers may be employed as a matrix in making up a friction particle containing other wear resistant materials such as brass particles, litharge and graphite. Thus fabricated friction

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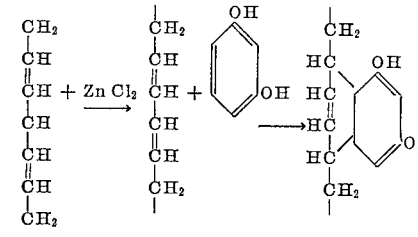
particles may then be bonded together with mineral fibers and strong heat and wear resistant binders such as a thermo-setting phenolic resin, to form a molded friction block. For the manufacture of friction particles, a major proportion of the liquid resorcinol-coupled fatty acid, or an incompletely hardened polymer thereof, may be mixed with heat and wear resistant mineral particles such as brass chips and litharge. Such mixing operation may be carried out on a hot roll rubber mill, and is followed by a baking operation to harden the product. The baked product is then disintegrated to a suitable size for use as a friction particle.

The primary polymerizable resorcinol-coupled fatty acids are made by reacting for a few few minutes at a temperature of approximately 200° C. substantially molecular proportions of resorcinol and of an unsaturated fatty acid such as linolinic acid, or of fatty oils such as linseed oil, soya bean oil, sardine oil or castor oil, in the presence of a dehydration type of catalyst such as benzene sulfonic acid or zinc chloride. For example, a fatty oil such as raw linseed oil, and resorcinol, are first mixed in the proportions by weight of about 100 parts fatty oil and 15 parts resorcinol. The mixture is heated to a temperature of about 125° C. in a vessel fitted with a stirrer, whereby to agitate the oil and dissolve the resorcinol in the oil. Benzene sulfonic acid or zinc chloride is then added to the mixture in amount ranging from 3 to 6% by weight of the mixture, and the source of heat is removed when the temperature of the mixture reaches about 125–130° C. On addition of the catalyst a vigorous exothermic reaction commences, which rapidly raises the temperature of the mixture; and accordingly the reaction vessel is preferably jacketed and temperature control is maintained, as by circulation of cooling oil through the jacket at a rate sufficient to prevent the reaction temperature from substantially exceeding an optimum temperature of 190–200° C. The reaction is allowed to proceed at this optimum temperature for about 20 minutes, at the end of which period a darkly colored viscous oil product is discharged from the reaction vessel. This viscous oil product is then preferably treated to effect removal of the catalyst, as by washing, or by dissolving in a varnish solvent and filtering.

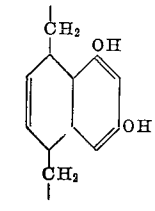
The coupling reaction between resorcinol and the fatty acid or fatty oil is preferably carried out in a vessel which is open at the top to atmosphere, to allow escape of water vapor which is liberated during the reaction. Instead of using an open vessel, an inert gas such as carbon dioxide or nitrogen may be circulated through a closed reaction vessel during the reaction, for the purpose of carrying off water vapor and any other volatile product of the reaction.

The liquid product of this initial condensation reaction differs markedly from the raw linseed oil or other fatty oil or fatty acid which is employed in its manufacture. As compared to the original fatty oil or fatty acid, this liquid reaction product has a somewhat higher saponification number, a much lower iodine number and a markedly higher acid or hydroxyl number. Whereas a raw linseed oil had a saponification number of 189, a hydroxyl number of 18.7 and an iodine number of 181, the product which was formed by reacting resorcinol with such raw linseed oil in the manner and proportions heretofore described, exhibited a saponification number of 192.5, an iodine number of 103, and a hydroxyl number of 45.3.

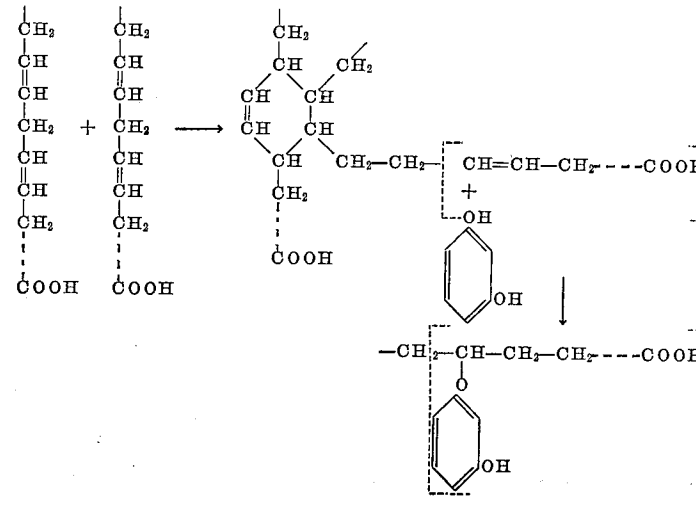
The primary resorcinol-coupled fatty oil or fatty acid which is employed as a binder, may be formed by a Diels-Alder type of reaction between the resorcinol and the fatty acid molecules at ethylenic linkages in the molecules, somewhat as portrayed in the following incomplete graphical formulas:



or



On the other hand, the resorcinol-coupled product may be formed by a reaction in which isomerisation first occurs between two molecules of fatty acid under the influence of the catalyst, followed by reaction of the resorcinol, somewhat in accordance with the following graphical formula:



When the reaction involves glycerides, the resorcinol-coupled product is capable of developing additional cross-linkages during the polymerization, with the final production of very tough and stable, strong cyclic molecules which are highly resistant to oxidation and to the effects of heat. Such strong cyclic structures are developed not only by heat polymerization, but also by reaction with aldehydes of the type of formaldehyde or furfural.

The primary viscous liquid resorcinol-coupled fatty acid is a heat sensitive material which can be polymerized by heat alone, such as 1–2 hours at 150–200° C., or by heat supplemented by reaction with small amounts of sulphur, paraformaldehyde or hexamethylene tetramine, to produce rubber-like solid polymers which resist deterioration or softening at temperatures as high as 230–240° C. and which are substantially water and oil insoluble and only about 10–15% soluble in acetone. This polymerized resin is much more heat resistant and is stronger and more durable than any products which can be produced by polymerizing fatty oils with zinc chloride in the absence of resorcinol. A solid polymer of the resorcinol-coupled linseed oil hereinbefore described had a saponification number of 191.3, a hydroxyl number of 39.1 and an iodine number of 76, whereas zinc chloride polymerized linseed oil, in the absence of resorcinol, exhibited a saponification number of about 210, a hydroxyl number of 8 and an iodine number of 95.

In the manufacture of fibrous heat and wear resistant products, the fiber component of the composition may be first fabricated into felted sheets or woven fabrics, and thereafter impregnated with the primary viscous resorcinol-coupled fatty oil; or the fibers may be first individually coated with the viscous oil, as by mixing in a Banbury mixer, and the resulting mixture then molded or sheeted out, as by extrusion, to a predetermined shape. Molding mixtures adapted for brake linings may comprise 30–60% by weight of asbestos fibers, 15–30% primary resorcinol-coupled linseed oil, 10–20% fine litharge, 4–5% barytes, 2–3% graphite, and 8–10 sulfur. The resulting impregnated sheets or molded shapes are finally baked to effect polymerization hardening of the resin binder.

Resorcinol-coupled linolenic and linoleic acids have the property of developing on polymerization a strong and tough bond for asbestos fibers and other mineral fillers. In order to obtain products of suitable moisture and chemical resistance, strength and wear resistance, the mixture of asbestos fibers and primary binder material is preferably subjected to a high compression and densifying operation to develop a strong physical bond between the binder and the asbestos fibers, and to force the binder within any interstices of the fibers. Commercial chrysotile asbestos fibers of the type normally employed in these compositions, consist of sheaves or bundles of fine fibers or filaments which are partially opened to such an extent that the resorcinol-coupled fatty acid binder may be forced under pressure into the openings between the individual fibers or filaments of the fiber bundles.

In some cases a solvent or partial solvent for the liquid resorcinol-coupled fatty acid (for example, petroleum naphtha) may be added during the mixing operation to reduce the viscosity of the primary binder and facilitate ready mixing of the binder with fibers and other pulverulent filler materials. This solvent is subsequently removed by volatilization during the final shaping and heat treatment or baking operations.

The primary liquid resorcinol-coupled fatty acid may be mixed with the asbestos fibers in a rubber-cement churn or Baker Perkins type mixer. Small amounts of sulphur and conventional rubber filling materials such as barytes and litharge may be incorporated in the mixture to form a thick plastic. The asbestos fibers are usually incorporated in amount representing 2–5 times the weight of the resorcinol-coupled fatty acid. The churn is operated until the batch is reduced to a fairly thin cement, before adding the asbestos fibers, and the mixture is thoroughly worked until the fibers are completely coated and their interstices impregnated with the cement compound. Due to adsorption of the cement by the fibers, the mass becomes a plastic dough, and in this form it may be banked between the heated rolls of a rubber calendering machine. Heated rolls are employed to effect evaporation of any varnish solvent employed in the mixture, whereby the tackiness of the mixture is increased and a strong adhesion is developed between the coated fibers and the surface of the hot roll. A dense film of the mixture is thus formed, and this film is built up to a tough resilient sheet of a thickness suitable for use as a packing sheet. A sheet thus formed is then cut from the hot roll and subjected to heat polymerization, preferably under pressure.

By baking the viscous liquid resorcinol-coupled fatty oil for a period of approximately 45 minutes at a temperature of 220° C., the oil is converted first to a soft sticky gel polymer, and finally to a hard solid rubberlike resin which is stable at temperatures as high as 250–350° C. Incorporation of asbestos insures heat stability at much higher temperatures. The solid products which result from straight heat polymerization of the liquid resorcinol-coupled fatty oil, or from heat polymerization supplemented by addition of formaldehyde, are substantially insoluble and resistant to disintegration by most common organic solvents and by water.

According to another modification of the method of manufacture, the primary viscous resorcinol-coupled fatty oil is first mixed with sulfur and fillers such as finely divided carbon, litharge and barytes, and the mixture is then polymerized to a tough, rubberlike product by a heat polymerizing treatment. This hard polymer is thereafter reduced to granular friction particle form and admixed with asbestos fibers and a thermo-setting type of phenolic or urea-formaldehyde resin, after which the resulting mixture is molded or otherwise shaped and subjected to a final molding and heat curing operation under pressure. Because of the matrix of resorcinol-coupled fatty oil in the friction particles, such particles when present as a major component of the final shape impart thereto a high degree of flexibility and resilience.

As illustrating the wear resistance of a solid heat polymerized resorcinol-coupled linseed oil product, such baked material was disintegrated and incorporated as friction particles in a friction material formula including approximately 30% of the hard polymerized resorcinol-coupled linseed oil, 10% brass chips, approximately 50% asbestos fibers and 10% heat hardenable phenol-formaldehyde resin. The thus formulated friction material mixture was then molded in a hot press mold at a temperature of approximately

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325° F. and under a pressure of about 2000 lbs. per square inch, to produce brake blocks which were tested for friction and wear characteristics. Brake blocks thus molded exhibited coefficients of friction approximating 0.32 and wear factors of .0028 cubic in./H. P. hr. by standard test methods, at a test temperature of 350° F. The above formula may be varied to include 15–30% by weight of the hard polymerized resorcinol-coupled linseed oil friction particles, 30–60% chrysotile asbestos, and 15–30% soft metal or other mineral fillers bonded with about 10% heat hardened phenol-formaldehyde resin.

A particularly efficient dielectric sheet suitable for wrapping cables or transformer coils has been made in accordance with the present invention by impregnating asbestos paper of 3–4 mil thickness with about 50% by weight of the primary viscous liquid resorcinol-coupled linseed oil produced by reacting linseed oil with resorcinol for 20 minutes by the method above described. Paper thus impregnated with the viscous oil diluted with a conventional varnish solvent, was baked for 45 minutes at a temperature of 170° C. The resulting impregnated and heat cured asbestos paper product exhibited a dielectric strength of upwards of 400 volts per mil thickness, a tensile strength of approximately 6 lbs. per square inch, and an elongation of approximately 4%. The impregnation treatment more than doubled the dielectric strength and tear resistance of the paper and increased the tensile strength by approximately 350%.

Since many variations may be made from the illustrative details given, without departing from the scope of the invention, it is intended that the invention should be limited only by the terms of the claims interpreted as broadly as consistent with novelty over the prior art.

What I claim is:

1. A heat and wear resistant article comprising mineral fibers and mineral particles bonded together in a hardened matrix of polymerized condensation product of resorcinol and an unsaturated fatty acid derivative of a fatty oil belonging to the group consisting of linseed oil, soya bean oil and castor oil, said article being characterized by stability and high wear resistance at temperatures of the order of 240° C.

2. A heat and wear resistant shape comprising a mixture of mineral fibers and friction particles bonded by a heat hardened and cured phenol-aldehyde resin, each friction particle comprising mineral filler particles suspended in a tough and resilient, matrix of heat cured polymerized resorcinol-coupled linseed oil, and said friction particles being present in the shape in major proportions sufficient to render the shape flexible and resilent.

3. A heat and wear resistant friction material comprising an intimate mixture of 15%–30% by weight of hard polymerized resorcinol-coupled linseed oil, 30%–60% chrysotile asbestos fibers and 15%–30% mineral filler bonded with about 10% heat hardened phenol-formaldehyde resin.

4. The method of manufacturing heat and wear resistant articles which comprises, forming a mixture incorporating 30–60% by weight of asbestos fibers, together with mineral filler particles, sulphur, and 15%–30% by weight of a liquid condensation product of resorcinol and a fatty oil belonging to the group consisting of linseed oil, soya bean oil and castor oil, and heating the resulting mixture to polymerize the liquid component to a heat and wear resistant solid.

5. The method of manufacturing molded friction shapes which comprises, forming a mixture consisting of 15%–30% by weight of liquid incompletely polymerized resorcinol-coupled linseed oil and heat and wear resistant mineral filler particles, baking the resultant mixture to produce a hard polymer, disintegrating the hard polymer to produce friction particles, admixing the friction particles with asbestos fibers and with a heat hardenable phenol-aldehyde resin, and molding the resulting mixture under applied heat and pressure sufficient to form a dense, hard product.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,262,887	Werner	Apr. 16, 1918
1,372,114	Baekeland	Mar. 22, 1921
1,766,932	Novak	June 24, 1930
1,961,177	Spokes	June 5, 1934
1,969,041	Seabury et al.	Apr. 7, 1934
2,047,149	Koenig et al.	July 7, 1936
2,059,260	Long et al.	Nov. 3, 1936
2,101,791	Ellis	Dec. 7, 1937
2,114,121	Bender	Apr. 12, 1938
2,154,969	Bender	Apr. 18, 1939
2,185,333	Denman	Jan. 2, 1940
2,317,487	Schuelke	Apr. 27, 1943
2,406,337	Auer	Aug. 27, 1946

OTHER REFERENCES

Oil, Paint and Drug Reporter, vol. 125, #6, page 24, February 5, 1934, 106–253.