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MANUFACTURE OF MATERIALS, BOARDS, ARTICLES, OR COMPOSITIONS OF A FIBROUS STOCK

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This invention relates to the manufacture of materials, boards, articles or compositions of a fibrous stock with a resinous composition in which non-acid fatty substances are saponified or emulsified, followed by hardening. The principal aim of the invention is to render the production more simple and cheaper, the resulting products having a greater mechanical strength and being more water repellant than those heretofore known.

The present application is a division of my copending application Serial No. 49,441, filed November 12, 1935.

I have discovered that resin soaps formed by saponifying phenolic resins in an aqueous alkaline solution, such as for instance solutions of KOH and/or NaOH, have the remarkable property of being capable of emulsification with a certain group of fatty substances which can only be dispersed with difficulty in solutions of resins in organic solvents. In the same manner a certain group of fatty substances may be saponified in the said alkaline resin solutions or may be mixed with soaps of such fatty substances. The fatty substances to which I refer are non-acid fatty substances, excluding fatty acids, and including saponifiable fats, oils, and waxes such as stearin, palmitin and castor oil; and unsaponifiable fats and waxes, such as wool fat, paraffin and ceresine. When I speak of "non-acid fatty substances", I mean such substances of fatty character capable of being dispersed or saponified in the aqueous alkaline liquid, so as to produce a homogeneous solution which contains the fatty substances in a finely divided state or in a clear solution and can be diluted with water to any desired extent.

I have further discovered that if base materials, such as wood, sawdust, wood meal, wood felt, sugar cane bagasse, pasteboard, cork meal, leather waste, and the like, are impregnated with aqueous alkaline liquids containing phenolic resins and the above-mentioned fatty substances, materials or articles having a substantially lower water absorbing capacity than those made by impregnation of such base materials with aqueous alkaline resin solutions not containing such fatty substances are obtained. The phenolic resin may also be mixed with soaps of natural resins. In this case the aqueous impregnating liquid consists of phenolic resins, soaps of natural resins and the said oils, fats, waxes, and the like, the latter being in an emulsified or saponified state.

My invention can be applied to materials containing a high percentage of water, without preliminary dehydration, because of the fact that impregnating solutions prepared in accordance with my invention are diluable to any extent with water without precipitation of the resins. For example, wood felt, which generally contains up to 80% of water as a result of the manufacturing process, can be commingled at once with my soap solution, without any intermediate steps.

As soon as the soap solution is incorporated with the base material, drying and hardening can be carried out in drying chambers at temperatures suited to the nature of the base material, preceded, if desired, by molding to give the material the required shape; or, the composition can be molded, dried, and hardened with the simultaneously application of heat and pressure, as described in the following examples.

By impregnating loose fibrous material with an aqueous alkaline solution of phenolic resin containing an addition of certain fatty substances, the resins and fatty substances being precipitated upon the fibrous material by the addition of metallic salts capable of forming insoluble precipitates with the resins and with the fatty substances. The resins and fatty substances being precipitated out of solution upon the fibrous stock, the liquid can then be removed from the mass in a mechanical way, as by draining upon a fine mesh sieve, with, or without suction, or pressure, or both, leaving slabs which can be sufficiently hardened for practical use by heating under such conditions as to harden the resin.

In consequence of the fact that the resin soaps used can be diluted with water to any desired extent, it is possible to make up compositions from pulverulant or fibrous materials with but a slight addition of resin soap, for example, 4% or less, with the advantage that the character of the fibrous stock is retained almost unaltered.

It is also possible, in accordance with my invention, to saponify those fats, oils and waxes which are capable of such reaction in the aqueous alkaline solution of phenolic resin, the substances being precipitated in the form of insoluble precipitates by the addition of the above-mentioned metallic salts.

It is found that the addition of the fatty substances makes the removing of the liquid from the stock quicker and more complete and particularly renders the finished articles more water repellant and consequently less subject to warping and attack by fungi.

The formation of insoluble precipitates of the resins, oils, waxes and fats by the addition of metallic salts capable of forming insoluble precipitates with the resins and with fatty substances

must take place only when the water is removed from the impregnated materials solely by drying without any mechanical operation. But when the water is removed from the impregnated materials by mechanical operations, for instance by sucking, pressing, calendering, centrifuging or the like, the resins and fats which are in a water soluble state as soaps or emulsions must be precipitated by addition of the said salts.

Under the action of vacuum and pressure, wood can be impregnated through its entire cross section with the solutions of the described nature, and then dried or hardened in the usual manner at normal or elevated pressure and temperature. In this manner the wood is not only preserved against decay but also improved, since its water repelling capacity and its strength are increased.

I have further found that textile fabrics can also be improved in quality by incorporating the described additions. After impregnation with the aqueous emulsions or aqueous solutions of soaps followed by precipitating on centrifuging or drying, or both, and calendering, these materials show considerably increased resistance to crumpling, water repellance, and resistance to tearing. Plies of material thus treated can be compressed singly or jointly by subjecting them to the simultaneous or successive action of pressure and heat, to form compositions.

To obtain, or to increase, non-inflammability in the final products, water soluble fireproofing agents, such as phosphates, sulphates, chlorides, bromides, acetates, and the like, as well as water glass, or a mixture of these substances, can be added to the impregnating medium. In the case of molded compositions, the fireproofness is increased by this expedient, while in the case of impregnated materials such as wood in the piece, textile fabric in lengths, and the like, fireproofing is effective without the interposition of separate steps in the manufacturing process. The salts used become deposited on the fiber and are not liable to become washed out.

The impregnated materials can also be treated with an aqueous solution of metallic salts, such as alum-, lead-salts, or the like for the precipitation of water insoluble compounds from the impregnating composition. It is possible by this treatment to produce, for example, loose boards or hard boards from wood pulp or similar material, by removing the water from the impregnated pulp through a fine mesh sieve and hot drying or pressing it. The fatty substances and the metal salts of the same respectively cause a more rapid dewatering of the pulp. The loose and hard boards have low water absorbing capacity, do not mildew and show high bending and tensile strength. If suitable salts, such as water soluble phosphates, borates, sulphates, chlorides, and the like be added to the fibrous material in the course of the described process, the resulting boards are also fire resistant in spite of their loose structure, while at the same time these last mentioned salts are almost proof against washing out.

When I speak of "phenolic resin" I refer to a hardenable synthetic resin which can be produced from phenol, or its polymers, particularly phenol (C_6H_5OH) or cresols ($C_6H_4.CH_3.OH$), and an aldehyde, particularly formaldehyde. Such hardenable resins become insoluble and infusible, when subjected to the action of heat or to the simultaneous action of heat and pressure. Such phenolic resins may be prepared by condensing phenol and the aldehyde in the heat and carrying the condensation to the point of separation of the reacting mixture into two layers. One example of a method for making such a condensation product is as follows:

1000 grams of cresol is mixed with 750 grams of 40% (volumetric) formaldehyde and heated in a reflux condenser. Before commencement of boiling of the mixture 5–10 grams of a condensing agent is added thereto. As condensing agent there can be used, for example, hexamethylenetetramine, soda, oxalic acid, and the like. Condensation can thus be effected either in the presence of alkalies, or in the presence of acids. Boiling of the mixture is then continued until the solution, after becoming turbid, separates into two layers. The condensation product is then dehydrated in vacuo at a temperature up to 90° C, and if necessary reheated at normal pressure until the product in the cold becomes so solid that it is brittle, hard, and similar in appearance to colophony.

For purposes of saponification, this condensation product is pulverized and saponified in the heat, for example, with caustic soda, 480 cc of caustic soda solution of 32° Bé being required for 1 kg of solid condensation product. A 20–30% aqueous start-solution of the said resin is made.

Substances which do not affect the valuable properties of the impregnating composition according to my present invention, may be added to the impregnating liquid.

The hardening process can be accelerated by the addition of various substances, such as alkali bichromate, manganese salts, and the like, which are known as oxidizers.

Examples of the process follow:

(1) 40–60 grams of a hardenable phenol-formaldehyde resin is dissolved in 1 litre of an aqueous solution containing 6–9 grams of NaOH, or 200–300 cc of the said start-solution are diluted with 700–800 cc of water. 15–25 grams of stearin or wool fat are emulsified in this solution suitably in the heat by the use of an emulsifying apparatus or saponified until a homogeneous solution is obtained. 1000 grams of wood meal is steeped in said emulsion, after which approximately 100 grams of ammonium phosphate dissolved in 200–300 cc of water is added to the mass. The resulting composition is dried and molded under a pressure of 285–350 lbs. per square inch at a temperature of 140–170°C.

(2) When asbestos powder is worked up the procedure followed may be the same as in example 1, 1000 grams of powdered asbestos being used instead of 1000 grams of wood meal. In this case the addition of ammonium phosphate can be dispensed with.

(3) 30–40 kg of a hardenable phenol-formaldehyde resin is dissolved in 1000 litres of an aqueous solution containing 4.5–6 kg of NaOH. 30–40 kg of palmitin are then incorporated with the solution (by treating as in example (1) until a homogeneous liquid is obtained). 35 cubic feet of wood in the piece is impregnated with 150–200 litres of said solution, the impregnation being assisted by alternate application of vacuum and pressure of 85–115 lbs/sq. in. The wood is then dried at normal or elevated temperature.

(4) 10–20 grams of a hardenable phenol-formaldehyde resin are dissolved in one litre of a solution containing 1½–3 grams of NaOH or 50–100 cc of the said start-solution are diluted with 900 cc of water. 5–10 grams of wool fat or stearin are then emulsified in the solution suitably in the heat by the use of an emulsifying apparatus or saponified until a homogeneous solu-

tion is obtained. Textiles (linen, cotton or artificial silk) are impregnated with said solution and then drawn through a 4–6% aqueous solution of borax or ammonium phosphate. Surplus solution is drained or centrifuged off and the material is calendered hot.

(5) To aqueous wood pulp 75–100 litres containing 1500 grams of dry wood, there is added 60–90 grams of the solid impregnating composition according to my present invention in the form of an aqueous liquid in the required state of dilution and the mass stirred in order to thoroughly mix the wood pulp with the impregnating composition. There is then added 100–200 cc of a 3% solution of an alum salt and stirring repeated. The mass is then dewatered upon a fine mesh sieve and hot dried to loose boards or pressed to hard boards or other articles by simultaneous application of heat and pressure.

In the above examples phenolic resin may be partly replaced by natural resin and the place of palmitin or stearin can be taken by other saponifiable substances, such as castor oil, or other oils or waxes, such as mining wax in suitable proportions. Instead of the non-saponifiable substance named in the examples there can also be employed paraffin, ceresine, or the like.

There are obtained products which are not substantially hygroscopic, which are readily workable and which are not attacked by insects, such as termites, nor by fungi. In the form of boards, for example, of half inch thickness, these products can be employed for building purposes and in the manufacture of furniture, the boards being used as a foundation for veneers of all kinds and qualities glued on with casein or other glues. One of the valuable properties of the specified soap solutions is that they are very well absorbed by the wood fiber itself, so that, for example, soft wood in the piece can be impregnated right through and then subjected to the hardening or drying process. The resulting product is impervious to moisture, of enhanced mechanical strength, readily workable, and excellently preserved.

It has been found that a fibrous material impregnated with an aqueous solution containing hardenable phenolic resins and non-acid fatty substances emulsified or saponified according to my present invention has a lower water absorption capacity than one containing only the resin compound. Samples of hard board were impregnated with an aqueous, alkaline solution of a hardenable phenol-formaldehyde resin only, without the addition of non-acid fatty substances, while other samples were impregnated under similar conditions with aqueous, alkaline solutions containing hardenable phenol-formaldehyde resin with the addition of increasing quantities of non-acid fatty substances. 6% of the impregnating composition—phenolic resin or phenolic resin+fatty substance—was incorporated in all the tests with the hard board. While the board treated with a solution of phenolic resin only, absorbed 6.0%, 21.7% and 29.8% water, respectively, after the sheets had been left lying in water for 2, 24 and 48 hours, the water absorption of the samples treated under similar conditions with compositions consisting of 90% (5.4% of dry fibres) phenolic resin and 10% (0.6% of dry fibres) wool fat, amounted to 4.6%, 15.7%, and 22.0% only. The expansion in length for these samples was, respectively, 0.064%, 0.379%, 0.411% and 0.061%, 0.317%, 0.347%; while the expansion in width was, respectively, 3.8%, 16.6%, 23.2% and 2.2%, 12.2%, 18.0%.

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