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PROCESS FOR THE PRODUCTION OF A BINDING AGENT FOR FIBROUS SUBSTANCES

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The present invention relates to the production of a binding agent, based upon sulphite waste liquor, for fibre substances of all kinds. This binding agent, because of its production and composition, is capable on the one hand of being mixed in desired concentrations with water to form a completely uniform stable emulsion and on the other hand of being precipitated from this emulsion by addition of suitable reagents and binding firmly to fibrous substances of all kinds in a finely divided disperse condition.

The technical, concentrated sulphite waste liquor from the sulphite cellulose process forms the starting material for the production of this binding agent. It is known that sulphite waste liquor is a good emulsifier for various organic products such for example as asphalt, tar, pitches, resins, oils, hydrocarbons etc. and that by its use aqueous dispersions of these products can be produced. These dispersions however do not possess the properties necessary for a good fibre binding agent, because the products which may be precipitated therefrom by coagulation do not bind adsorptively onto the fibrous substances, but after coagulation has been effected by addition of suitable substances remain freely suspended in the liquid containing the fibrous substance and upon separation of this liquid from the fibrous substance are for the greatest part separated with the liquid.

The employment of sulphite waste liquor as starting material for the production of a binding agent for fibrous substances would also have been regarded as impracticable because it was known that the sulphite waste liquor is very readily decomposed by addition of coagulant substances such as acids or acid salts, the ligno sulphonic acid being precipitated with splitting off of free acetic acid. Here however it is precisely the organic complex, namely the lignosulphonic acid, the preservation of which represents an essential feature for the technical success of the binding agent according to the invention, which is destroyed.

It has now been found that it is possible in the following manner to build up from sulphite waste liquor a binding agent in which the sulphite waste liquor is protected on the one hand from decomposition by the action of the precipitating reagents and on the other hand is so closely combined with the additional substances distributed therein that upon precipitation of this binding agent from its aqueous emulsion no separation of the sulphite waste liquor from the additional substances takes place. The substances contained in the sulphite waste liquor, particularly the lignosulphonic acid, remain on the contrary in fixed chemical combination with the addition substances precipitating and are precipitated together with the latter upon the fibrous substance in finely disperse form. This effect is obtained by the following treatment of the sulphite waste liquor.

The technical, concentrated sulphite solution is first mixed with albumen or albumen-containing substances or solutions or emulsions thereof. Products such as yeast, yeast-like substances, milk, casein and the like come into consideration as such albumen-containing substances. The addition of these substances effects the stabilisation of the sulphite waste liquor against the decomposing action of precipitating agents.

Further, the sulphite waste liquor has added to it an addition of aromatic amines, mono-, di- or polyamines or derivatives thereof by way of example aniline, phenylene diamine or the like. These additional substances serve the purpose of chemically binding the sulphite waste liquor complex to the organic substances to be distributed in it, and in this way it is ensured that these substances upon subsequent addition of precipitating reagents are not precipitated by themselves, but because of their linkage effected through the aromatic amines onto the sulphite waste liquor complex the latter is precipitated in association with them.

Organic substances, which together with the sulphite waste liquor complex form the binding agent according to the invention, are now introduced by simple stirring and emulsifying, preferably with simultaneous moderate heating to about 60°C, into the sulphite waste liquor prepared in the above manner and containing the albuminous substances and aromatic amines. As such substances there preferably come into consideration phenol-aldehyde resins in the resol condition, heat-hardenable carbamide resins, bitumens, drying oils, hydrogenated fatty alcohols or fatty acids, phenols in the presence of aldehydes, metal soaps of fatty acids or resins, tars, especially wood tar, asphalt, glue, casein or similar protein substances etc. singly or in admixture with one another. The choice of these additional substances or mixtures thereof as regards composition and quantitative proportions depends upon the particular requirements which are to be made upon, and are to be fulfilled by, the fibrous substance product produced with employment of the binding agent.

The binding agent is ready when the last men-

tioned additional substances have been introduced. It represents a thickly liquid, highly viscous, liquid mass which is more or less dark coloured according to the type of the additional substances and is indefinitely stable without decomposition and may be distributed in water to form an entirely homogeneous milk-like emulsion in any desired quantitative proportions, even at very high dilutions.

The precipitation of the binding agent upon dispersed fibrous substances of desired kind is undertaken in manner known per se as follows:

The binding agent according to the invention is added in desired quantity to a paste of fibrous substance dispersed in water. The said quantity may amount to a few per cent. calculated upon the solid fibrous substance; it can however be increased to higher percentages, to about 40% when the demands upon the finished product so require. After addition of the binding agent the paste of fibrous substance represents a milky liquid in which the fibres are distributed. The precipitation of the binding agent is effected by addition of acid reacting water-soluble substances. The addition of a mixture of equal parts of aluminium sulphate and zinc chloride is particularly suitable. However other acid reacting salts, inorganic acids in appropriately low concentrations, or organic acids such as lactic acid and the like may also be employed as precipitating agents.

Upon addition of these precipitating reagents. deposition of the binding agent milkily dispersed in water immediately takes place in finely distributed disperse form upon the surface of the fibres. It is characteristic and decisive for the technical value of the binding agent according to the invention that the entire complex of the binding agent, including the high molecular substances contained in the sulphite waste liquor, precipitates upon the fibres, so that the fibres loaded with the binding agent are now suspended in a clear watery liquid containing substantially only water-soluble low molecular components of the binding agent and the other additions.

The paste of fibrous substance loaded with the binding agent can now be brought into the paper machine and worked up to paper, board, and the like in the usual manner. The finished products thus produced show considerably better mechanical properties, in particular greatly improved tensile strength, compared to products produced with employment of the previously known binding agents.

It has further been found that products of outstanding excellence and quite unusual mechanical properties, in particular having strengths hitherto not attained in this field, can be produced in that the fibrous substance loaded with the binding agent, after removal of the aqueous liquid and forming into layers upon the paper machine, are dried and subjected to hot pressing in manner known per se. In this way shaped bodies may be produced of desired form, preferably plates, rods, tubes, beams etc. which as regards mechanical strength surpass the previously known pressed materials of fibrous substance and in many ways are suitable for replacing wood, especially plywood and similar improved products as well as many metals. The pressed bodies produced may on the one hand be treated, drilled, sawed etc. like wood and on the other hand are to a high degree indifferent chemically and physically.

The following examples illustrate how the invention may be carried into effect:

1. 1000 parts of concentrated sulphite cellulose waste liquor of about 30° Be are stirred with 100 parts of yeast or yeast-like products, which are dissolved in 100 parts water, and with 100 parts of aniline. The mixture is heated to about 60°C. and combined with stirring with 10% of its total weight of a phenoplastic resol or a carbamide resin or a mixture of these two. 150 parts of glutin (glue) are swelled and melted in 150 parts of water and 30 parts of a fatty alcohol mixture of 15 parts glycerine and 15 parts cetaceum are introduced into the melt. The mixture is carefully heated and emulsified with 30 parts of birch tar. Thereupon it is combined hot with the sulphite waste liquor mixture and stirred. The thickly liquid mass obtained is indefinitely stable and may be distributed in water in any proportion to form a homogeneous dispersion.

2. 500 parts of anhydrous sulphite cellulose waste liquor, that is to say the same in dry powder form, are introduced into and stirred with 500 parts of skim milk, in which 10 parts of β-naphthol and 10 parts of pepsin have previously been dissolved. After uniform distribution 100 parts of aniline are further introduced and the mixture is once more vigorously stirred. The mixture is heated to about 50–70° C. and combined with stirring with 10% of its total weight of a phenoplastic resol or a carbamide resin or a mixture of the two. 100 parts of colophonium are ground to powder with 50 parts of high melting mineral oil bitumen in a colloid mill and combined hot with stirring with the above sulphite waste liquor mixture.

3. 1000 parts of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products together with 100 parts by weight of aniline. 100 parts by weight of glutin are melted in 200 parts by weight of water and mixed with 300 parts by weight of phenol or cresol and with 100 parts by weight of birch-tar. The whole is stirred for so long with heating until a completely homogeneous mass has been produced. After cooling to room temperature 200 parts by weight of a 40% aqueous solution of formaldehyde are added. The mass is then stirred for so long whilst heating moderately once more until the smell of formaldehyde has disappeared.

4. 1000 parts by weight of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products as well as 100 parts by weight of aniline. 300 parts by weight of carbamide resin, 50 parts by weight of fatty alcohol consisting of 25 parts glycerine and 25 parts cetaceum, and 200 parts by weight of a 40% aqueous solution of formaldehyde are added. The whole mixture is stirred for so long with moderate heating until a uniform homogeneous mass has been produced.

5. 1000 parts of concentrated cellulose waste liquor are combined with stirring with 100 parts by weight of yeast or yeast-like products and 100 parts by weight of aniline. 150 parts by weight of phthalic acid anhydride are condensed with 150 parts by weight of glycerine and to this there are added 100 parts by weight of stearic acid and 250 parts by weight of colophonium ground in a colloid mill, which have previously been partially saponified by addition of 250 parts by weight of a caustic potash solution of 8°Bé. The whole mixture is stirred for so long with moderate heating

until a uniform homogeneous mass has been produced.

6. 150 kgs. of ground wood fibres (white ground wood and brown ground wood) are distributed in 3 cbm of water and mixed in a Hollander with 25 kg. of the binding agent produced as described in example 1 or 2. Hereupon 10 kgms. of a weakly acid precipitating liquid, consisting of 3 parts of aluminium sulphate and 3 parts of zinc chloride dissolved in 4 parts of water, are added, whereby the binding agent is precipitated upon the fibres. The paste of fibrous substances containing the binding agent is then separated upon a paper-making machine from water by means of suction and dried at a temperature of about 100°C. to laminar bodies about 2.5 cms. thick. These laminar bodies are then pressed upon heated hydraulic plate presses at a temperature of 140–150°C and a pressure of about 60–70 kgms/cm² for a few minutes into finished pressed plates of about 8 mms. thickness. The pressed plates so produced are extremely suitable for substitutes for plywood. The mechanical strengths of such pressed plates reach the following values calculated as averages:

Compressive strength	about 2000 kgms/cm²
Bending strength	about 500 kgms/cm²
Tensile strength	about 350 kgms/cm²
Impactive bending strength	about 8 cmkg/cm²
Ball pressure hardness after 10 secs	about 3000
Ball pressure hardness after 60 secs	about 2500

When employing long-fibred ground wood the values for the bending and tensile strengths increase by about 40–50%.

7. 150 kgms. of washed ground wood (that is freed from adhering cementing substance) is mixed with 3 cbm of water and 35 kgms. of the binding agent produced as described in examples 1 or 3 and the binding agent is then precipitated upon the fibre substance with 20 kgms. of a weakly acid reaction liquid consisting of 6 parts of aluminium sulphate and 6 parts of zinc chloride dissolved in 12 parts of water. The further treatment of the paste of fibrous substance containing the binding agent as far as its conversion into dried laminar bodies takes place as in example 6.

The laminar bodies of about 2.5 cms. thickness thus produced are then pressed upon hydraulic heated plate presses at a temperature of 150–160°C. and a pressure of 80–100 kgms/cm² to form pressed plates of about 6 mms. thickness. The plates thus produced may be employed for example as insulating pressed substances in the electrical art, as substitutes for various kinds of metal (bushings, toothed wheels etc.) substitutes for metal foils etc. The mechanical strengths in this case reach the following values calculated as averages:

Compressive strength kg/cm²	about 2750
Bending strength kg/cm²	about 800
Tensile strength kg/cm²	about 500
Impactive bending strength cmkg/cm²	about 10
Ball pressure hardness after 10 secs	about 3800
Ball-pressure hardness after 60 secs	about 3300

In this case also when employing long-fibred fibrous substances the tensile and bending strengths are considerably increased.

It is already known that aqueous emulsions of artificial resins or the like can be employed for steeping fibrous substances. By way of example an aqueous artificial resin emulsion produced with employment of gum arabic has been employed for this purpose. Such an emulsion does not however give up its content of artificial resin or other substances distributed in it to the fibrous substance so that on separating the liquid from the fibrous substance only those components of the artificial resin which correspond to the quantity of liquid retained by the paste of fibrous substance by absorption remain behind in the fibrous substance, in an irregular distribution and not bound to the fibrous substance. In this case therefore a very considerable proportion of the amount of additional substance dispersed in the liquid goes to waste unused.

In order to remove this disadvantage it has also already been proposed to employ emulsions or solutions of subtsances which may be caused to separate by addition of precipitatingly acting emulsion destroyers and thus to deposit upon the fibre the additional substance contained in the emulsion or the solution. The results obtained in this way are thoroughly useful as such and the process of depositing the substances contained in the emulsion corresponds to the method of working described above. The essential difference and the consequent technical advance of the present process depends, in contradistinction to the above, upon the use of the binding agent according to the invention. It was not known on the one hand that such binding agent emulsions could be built up upon the basis of sulphite waste liquor, and above all it was not known that such a binding agent could be so built up that not only the emulsified additional substances but above all also the emulsifier, that is to say the sulphite waste liquor or the high molecular substances contained therein, can be carried down upon precipitation and a fibrous substance loaded with binding agent thus be produced from which finished products of quite unusual mechanical and other properties can be produced. In particular also, the production of shaped bodies by heat and pressure from a fibrous substance loaded with a binding agent containing sulphite waste liquor was not known.

Finally it was also previously known that sulphite waste liquor can be condensed with phenols, amines or urea, upon the one hand and with aldehydes or ketones on the other hand, and thereby products be obtained which are water-soluble and soluble in various reagents, mostly alkalis. These products however are not binding agents of the same type as those herein described, since they are not precipitated from their solutions in a form adhering to the fibre. Such solutions on the contrary precipitate the substance which they contain in a freely suspended form not bound to the fibre and the technical effects of such products as binding agents are therefore insufficient. These known products may at the best be employed as adhesive substances, tanning agents and the like. They do not on the other hand represent a binding agent of high affinity for fibrous substances, which gives great mechanical strength to the finished products.

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