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TREATMENT OF FIBROUS MATERIALS WITH COATING OR IMPREGNATING AGENTS

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This invention relates to the treatment of fibrous substances with the object of coating or surrounding the individual fibres or bunches of fibres with a water insoluble fibre-coating substance or with fibre-coating substances capable of being rendered substantially insoluble in water whereby such fibres can be subsequently formed into a sheet or board on the normal paper making or board making equipment or can be separated from the water and compressed and moulded by pressure.

Within the term "water insoluble fibre-coating substance" in the present invention are included all those fibre-coating substances insoluble in water or capable of being rendered insoluble in water which are in the form of "an aqueous dispersion or emulsion" in the natural state or are capable of being made into a dispersion or emulsion in water. Within the term "aqueous dispersion or emulsion" are included systems in water containing particles of solid or liquid stabilised by any of the known protective agents stable under both acid and alkaline conditions and in the presence of metallic salts, but exclude those systems stabilised by cationic soaps to give dispersions or emulsions having particles possessing a positive charge of electricity. Typical examples of known protective agents are the fatty alcohol ethylene oxide condensate known as Lubrol W and the sodium salt of alkylated naphthalene sulphonic acid known as Perminal BX.

A wide variety of water insoluble fibre-coating substances may be used dispersed or emulsified in water and the following types of aqueous dispersion are given as illustrative of but not limitative of the scope of the invention:

Rubber latex either naturally occurring or made by redispersing solid rubber, vulcanised and unvulcanised and latices of the following substances:

Polyvinyl chloride, polyvinylidene chloride, co-polymers of vinyl chloride and vinylidene chloride polyvinyl acetate, co-polymers of vinyl acetate and vinyl chloride, polyacrylates, polymethacrylates and co-polymers thereof; poly-isoprene, polychloroprene, co-polymers of butadiene and styrene, co-polymers of butadiene and acrylonitrile, polystyrene, linseed oil, rosin, alkyd resins, ester gum, paraffin wax, petroleum jelly, carnauba wax, microcrystalline waxes, asphalt, tar, pitch, bitumen and terpene resins, phenol formaldehyde, urea formaldehyde, melamine formaldehyde, resins and polyester resins.

Mixtures of various latices may also be used, for example—dispersions of vinyl polymers or co-polymers with dispersions of butadiene acrylonitrile co-polymers.

In the normal paper making processes, it is usual to suspend fibres by beating for example and to add thereto aqueous dispersions or emulsions of water insoluble fibre-coating substances or fibre-coating substances capable of being rendered substantially insoluble in water. A coagulant such as alum is then stirred in with the object of breaking the dispersion or emulsion so that the particles agglomerate and become deposited on the fibres.

Since however coagulation occurs in the aqueous phase, considerable agglomeration takes place before deposition on the fibre with the result that the water insoluble fibre-coating substance may be deposited on the fibres in relatively large lumps, or may not adhere to the fibres at all. It has also been found difficult to achieve uniform coating of the fibres by the means just described. Another known method is to add to the fibres, suspended in water a coagulant such as alum and then run this mixture into the aqueous dispersion or emulsion as previously described. In both methods coagulation occurs before deposition on the fibre. By the process of the present invention coagulation of the dispersion of water insoluble fibre-coating substance is effected at the surface of the fibre and there is a progressive build up of coagulum on the fibre until the dispersion is completely exhausted of water insoluble fibre-coating substance. In this way the fibres are evenly and uniformly coated.

Of the known coagulants for aqueous dispersions some are effective immediately on coming into contact with the aqueous dispersion, for example acids and certain salts. Others have a delayed action whereby intimate mixing of the delayed action coagulant and aqueous dispersion can be effected and the coagulation follows after an interval of time; while a third type known as heat sensitive coagulant can be mixed into the aqueous dispersion and coagulation will not occur until the mixture is heated, for example above 15° C.

Some of these heat sensitive coagulants decompose on heating to liberate acid and thereby bring about coagulation. Some, very sparingly soluble at room temperature, may be added as a dispersion and then on heating dissolve and cause coagulation. Some quite soluble at room temperature, become less soluble at elevated temperatures. This last mentioned class of heat sensitive coagulants is particularly suited to the process of the present invention. This class is referred to herein as a polymeric heat sensitive coagulant and is herein defined as an organic compound containing an ether linkage R—O—R′ in which R is a polymeric group and R′ an alkyl or aryl group and is characterised in that it is soluble in water at a given temperature and becomes insoluble at an elevated temperature. By the term "elevated temperature" is meant that temperature at which the solubility in water of the polymeric heat sensitive coagulant becomes so low that precipitation occurs. A typical example of such a coagulant is polyvinyl methyl ether, which is soluble in water at 20° C. but becomes much less soluble within the temperature range from 30 to 40° C. and is precipitated.

From one aspect the present invention may be considered as consisting in adding to a suspension of fibres in water a polymeric heat sensitive coagulant of the kind herein defined and heating the suspension to an elevated temperature whereby the fibres are conditioned for the subsequent deposition thereon of a water insoluble fibre-coating substance from an aqueous dispersion of the substance.

From another aspect the invention may be considered as comprising the coating of fibres suspended in water with a polymeric heat sensitive coagulant as herein defined and adding thereto an aqueous dispersion or emulsion of a water insoluble fibre-coating substance in the presence of an acid or acidic substance or salts of tri- or polyvalent metal and a protective soap in such proportions and under such conditions of temperature that the water insoluble fibre-coating substance is deposited on the fibre in a uniform manner.

The mixture of fibrous material, acid, acidic substance or a salt of a tri- or polyvalent metal and the heat sensitive coagulant is however heated, then cooled

prior to the addition of the aqueous dispersion of water insoluble substance, and re-heated after the addition.

The essential feature of the process is the addition of a polymeric heat sensitive coagulant to the suspension of fibres in water and heating to an elevated temperature before the addition of the aqueous dispersion of water insoluble fibre-coating substance. This is to ensure that coagulation occurs at the fibre and the water insoluble fibre-coating substance is deposited thereon.

Various fibres both natural and synthetic such as cellulose, wood, jute, hemp, sisal, manila, wool, rayon, nylon, leather, asbestos, glass and mixtures thereof may be treated by the process according to the present invention.

A preferred mode of carrying out the process of the invention is as follows:

The fibre is beaten with water to give a uniform suspension which is then treated with acids or acidic substance or a salt of a tri- or polyvalent metal such as aluminum sulfate, hereinafter referred to as alum. A polymeric heat sensitive coagulant having the property of becoming insoluble in water at temperatures above 30° C. for example, polyvinyl methyl ether, is then mixed into the suspension of fibre in water and the whole mixture heated to a temperature above 30° C. with the object of depositing the polymeric heat sensitive coagulant on the fibre. The mixture is then cooled below 30° C. and an aqueous dispersion or emulsion of water insoluble fibre-coating substance containing a suitable protective agent such as anionic or non-ionic soaps stable under alkaline and acid conditions and in the presence of metallic salts, is added. No coagulation of the dispersion takes place under these conditions but on subsequent re-heating above 30° C. the water insoluble fibre-coating substance is deposited on the fibre in a uniform manner.

We have found that this procedure may be varied in the following ways:

The process as previously described can be carried out up to the point where the mixture of water, fibre and polymeric heat sensitive coagulant is heated to a temperature above 30° C. at which point the particular aqueous dispersion of water-insoluble fibre-coating substance is added and partial coagulation occurs. It has however been found necessary to cool the mixture and re-heat to a temperature above 30° C. to effect complete deposition.

The process may be further modified by adding the acids, acidic substance or salt of tri- or polyvalent metal with the aqueous dispersion of water insoluble fibre-coating substance suitably protected by soap instead of adding it to the fibre in the first step of the process.

Although the preferred method results in a more uniform deposition of water insoluble substance on the fibre, and is easier to control, the other methods give a product from which it is possible to form a sheet or mass having useful properties.

The acid or acids, acidic substance or salt of tri- or polyvalent metal and protective soap are used with the object of preventing coagulation of the aqueous dispersion of water-insoluble fibre-coating substance prior to heating yet at the same time permitting it at the elevated temperature.

The choice of acid or metallic salts is determined by the type of aqueous dispersion of water-insoluble substance to be used. Certain naturally occurring rubber latices are readily coagulated by small amounts of acid whereas some synthetic dispersions contain considerable amounts of protective agent, included during manufacture, and are not readily coagulated by acid but can be coagulated by metallic salts such as alum.

Again the type of protective soap to be used is influenced by the choice of acid or metallic salt. Anionic soaps derived from fatty acids by neutralisation with sodium or potassium or ammonium hydroxide are not suitable since they have no protective action under acid conditions or in the presence of certain metallic salts.

Anionic soaps containing sulfonic acid groups neutralized by sodium, potassium or ammonium hydroxides are stable under acid conditions and therefore can be used with acid but they are not suitable for use with salts of tri- or polyvalent metals.

Non-ionic soaps can be used with acids or salts of tri- or polyvalent metals. A typical example is a fatty alcohol ethylene oxide condensate known as Lubrol W.

The amount of acid or acids, acidic substance or tri- or polyvalent metal used in any of the methods just described can be varied between wide limits. Furthermore the amount so used affects the quantity of protective soap to be used and in turn controls the amount of polymeric heat sensitive coagulant required.

The following table shows the range of proportions of these ingredients that can be used with wood fibre, all parts being dry weight:

TABLE 1

	A	B
Wood fibre	100	100
Aqueous Dispersion of Rubber or Resin	50	50
Alum	100	2
Polymeric Heat Sensitive Coagulant	15	3
Non-ionic Soap (Lubrol W)	10	1

Columns A and B represent the broad limits within which these ingredients may be varied. Furthermore the type of fibre and the particular aqueous dispersion of water-insoluble fibre-coating substance used influences the amounts of the various ingredients required and it is necessary to carry out a series of experiments to determine the preferred amounts. It is found that the best procedure is to start with a large amount of alum and use the proportions shown in column A for the various ingredients. The alum is then progressively reduced with proportionate decreases in the quantity of protective soap and polymeric heat sensitive coagulant. There is not a strictly proportional relationship between these ingredients and it may be necessary to vary one or other. Columns A and B are intended to show the approximate proportions required. The amount of acid required can be determined by a similar procedure.

In the following examples of the process all of the parts are by weight.

Example I

5 parts of wood fibre are beaten into a suspension with 1000 parts of water. This suspension is then acidified to a pH of 3.5 with 20 parts of alum solution containing 20 parts of aluminum sulfate in 80 parts of water. 5 parts of a solution containing 15 parts of polyvinyl methyl ether in 85 parts of water are added to the acidified suspension and the whole is heated to 35° C. with gentle agitation. When this temperature is attained the suspension is cooled down and the following mixture added:

8 parts of an aqueous dispersion consisting of 40 parts of butadiene acrylonitrile co-polymer and 60 parts of water,

5 parts of a solution of a non-ionic soap such as Lubrol W containing 10 parts of soap in 90 parts of water.

100 parts of water.

The suspension is then re-heated to 35° C. with gentle agitation and the resulting treated fibre formed into sheet by removal of the supernatant liquor.

Example II

5 parts of ground leather is beaten into a suspension with 1000 parts of water. The fibre is detanned by adding .5 part of ammonia S.G. 880 such that the suspension acquires a pH of 7.5. The suspension is adjusted to pH

3.5 with a solution of alum containing 20 parts of aluminum sulfate in 80 parts of water.

5 parts of a solution containing 15 parts of polyvinyl methyl ether in 85 parts of water are added to the acidified suspension and the whole is heated to 35° C. with gentle agitation. When this temperature is attained the suspension is cooled down and the following mixture added:

8 parts of an aqueous dispersion consisting of 40 parts of butadiene acrylonitrile co-polymer and 60 parts of water,
5 parts of a solution of a non-ionic soap such as Lubrol W containing 10 parts of soap in 90 parts of water.
100 parts of water.

The suspension is then re-heated to 35° C. with gentle agitation and the resulting treated fibre formed into a sheet by removal of the supernatant liquor.

Example III

5 parts of wood fibre are beaten into a suspension with 1000 parts of water. This suspension is then acidified with 10 parts of alum solution containing 10 parts of aluminum sulfate in 90 parts of water. 2 parts of a solution containing 10 parts of polyvinyl methyl ether in 90 parts of cold water are added to the acidified suspension and the whole is heated to 35° C. with gentle agitation. When this temperature is attained the suspension is cooled down and the following mixture added:

5 parts of natural rubber latex consisting of 60 parts of Hevea rubber and 40 parts of water,
1 part of a 4% solution of formaldehyde in water,
6 parts of a solution of a non-ionic soap, a fatty alcohol ethylene oxide condensate known as Lubrol W containing 1 part of Lubrol W in 99 parts of water,
100 parts water.

The suspension is then re-heated to 35° C. with gentle agitation and the resulting treated fibre formed into a sheet by removal of the supernatant liquor.

Example IV

5 parts of long fibre asbestos is beaten into a suspension with 1000 parts of water. This suspension is then acidified to a pH of 3.5 with 20 parts of alum solution consisting of 20 parts of aluminum sulfate and 80 parts of water. 5 parts of a solution containing 15 parts of polyvinyl methyl ether in 85 parts of cold water are added to the acidified suspension and the whole is heated to 35° C. with gentle agitation. When this temperature is attained the suspension is cooled down and the following mixture added:

6 parts of an aqueous dispersion consisting of 40 parts of butadiene acrylonitrile co-polymer and 60 parts of water.
6 parts of solution containing 1 part of Lubrol W in 99 parts of water.
100 parts of water.

The suspension is then re-heated to 35° C. with gentle agitation and the resulting treated fibre formed into a sheet by removal of the supernatant liquor.

Example V

5 parts of wood fibre are beaten into a suspension with 1000 parts of water. This suspension is then acidified with 10 parts of aqueous solution of acetic acid strength 4 Normal. 6 parts of a solution containing 10 parts of polyvinyl methyl ether in 90 parts of cold water are added to the acidified suspension and the whole is heated to 35° C. with gentle agitation. When this temperature is attained the suspension is cooled down and the following mixture added:

5 parts of natural rubber latex consisting of 60 parts of Hevea rubber and 40 parts of water,
1 part of a 4% solution of formaldehyde in water,
5 parts of a solution of an anionic soap containing 5 parts of Perminal BX in 95 parts of water,
100 parts of water.

The suspension is then re-heated to 35° C. with gentle agitation and the resulting treated fibre formed into a sheet by removal of the supernatant liquor.

The phrase "water-insoluble fibre-coating substance" as used in the specification and claims is intended to include fibre-coating materials of the types and kinds listed in the specification as well as other materials used for coating fibres in aqueous suspension, particularly where the resulting coated fibres are subsequently formed into a bonded material, such as a sheet or board.

We claim:

1. In the method of coating fibres in which a water-insoluble fibre-coating substance is deposited on the fibres from an aqueous dispersion thereof, the steps which comprise forming an aqueous dispersion of the fibres to be coated and a polymeric heat-sensitive coagulant for the fibre-coating substance comprising a polyvinyl alkyl ether, said polyvinyl alkyl ether being decreasingly soluble in water as the temperature of the water is raised, heating said dispersion to a temperature sufficiently high to precipitate polyvinyl alkyl ether therefrom with resultant deposition of said polyvinyl alkyl ether on said fibres, and thereafter adding to the resultant dispersion of fibres an aqueous dispersion of the water-insoluble fibre-coating substance.

2. In the method of coating fibres as set forth in claim 1 in which the suspension, after being heated to precipitate polyvinyl alkyl ether with resultant deposition thereof on the fibres, is cooled to a temperature below that at which polyvinyl alkyl ether was precipitated therefrom, and the aqueous dispersion of the water-insoluble fibre-coating substance is added to the cooled dispersion, and the dispersion thereafter is reheated to said temperature at which polyvinyl alkyl ether was precipitated therefrom.

3. In the method of coating fibres as set forth in claim 1 in which the aqueous dispersion of the fibres is acidified and the aqueous dispersion of the water-insoluble fibre-coating substance which is added to the aqueous dispersion of fibres contains a protective soap.

4. In the method of coating fibres as set forth in claim 1 in which the polyvinyl alkyl ether is polyvinyl methyl ether.

5. In the method of coating fibres as set forth in claim 4 in which the aqueous dispersion containing the fibres and the polyvinyl methyl ether is heated to a temperature of about 35° C. to precipitate polyvinyl methyl ether therefrom.

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