PROCESS OF LOADING CELLULOSIC FIBERS


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This invention relates to the treatment of cellulose fibers notably those used in the manufacture of various types of paper and fiberboard whether prepared on a customary paper making machine by a felting process or on textile machinery, such as employed for producing so-called non-woven fabrics.

With respect to the cellulose fibers, the invention is applicable to all ordinary paper pulps as well as chemically treated fibers and synthetically prepared fibers. For example, the invention is useful in connection with pulps prepared from ground wood or kraft pulp, as well as pulp prepared by the sulfate and sulfite processes and also regenerated cellulose.

The primary object of this invention is to produce a combination of resin and fiber in which the resin is completely, uniformly, firmly and permanently adhered to the individual fibers and is distinguished from ordinary products by the substantially complete absence of discrete resin particles held mechanically in the fiber interstices (which latter condition is objectionable because it leads to non-uniform disposition of resin with respect to the cross section of the paper sheet).

An object of this invention is to obtain a coating on the fibers which will be permanently adhered, abrasion resistant, and which will be distinguished from ordinary products in that instead of the coating on the fibers existing as a coagulated mass, the coatings produced according to the present invention can be readily identified by presenting a uniformly adhered coating on the individual fibers which, in the final product, will be present uniformly throughout the cross section of the thickness of paper or paper board.

Another object of the invention is to provide a method which will be readily adaptable to paper making practice and can be used with existing paper making machinery. In this connection, it is a further object of the invention to provide a method which will not be injurious to such paper making machinery, and will not require the frequent cleaning to which such machinery is subject in present-day operations where, for example, certain synthetic resins are embodied in the paper pulp.

An equally important object of the invention is to provide a method in which the relatively expensive coating materials are used with optimum efficiency as is best demonstrated by the elimination of waste byproducts encountered. That is to say, an examination of the usual white water from a paper making operation, during the use of the present invention, discloses substantially no resin present.

It is an additional object of the invention to increase enormously the amount of resin which can be incorporated within the body of the sheet over what has heretofore been possible by conventional operations, and this increase is brought about uniformly within the cross sectional area of the sheet. It results in sheets having good "formation" without producing undue smoothness of the stock, and sticking or clogging of the paper making machinery.

Another object of the invention is to provide a method wherein the individual fibers are so uniformly coated that the completed sheet exhibits not only an increased tear strength and burst resistance, but these attributes are uniformly found throughout the area as well as cross section (thickness) of the sheet. Such an improved sheet is to be distinguished from the usual resin saturated or impregnated sheets or sheets made by present beater or head box addition practices, wherein there is a tendency for the impregnating material to accumulate on the surfaces and adjacent the surface zone due to the filtering action of the paper structure which will result in weakening the sheet and also producing objectionable splitting of the sheet.

It has been observed that paper stock treated in accordance with this invention is produced without sacrificing freeness and in some cases the freeness of the stock is improved. When the stock is laid down upon the screen or wire of a web forming instrumentality, it does not exert any tendency to penetrate through the same nor stick.

To one skilled in the art of paper making, these features are of marked significance.

In carrying out the invention, it will be illustrated in connection with an aqueous slurry of paper fibers such as are to be found in the usual processes for reducing pulp to a desirable fiber structure. It is to be understood that the same steps will be utilized in connection with any of the other types of cellulosic fibers.

A slurry of cellulosic fibers, for example, ordinary paper pulp is produced in the paper beater and to this slurry there is added a cationic coupling agent which is the alkylated amidation product obtained by reacting polyamine with a fatty acid or a dicarboxylic acid and then reacting with a suitable alkylation compound. The particular pulp is tested in order to determine its capacity to exhaust or absorb the cationic active compound and then an amount of the latter is added to the slurry which will be exhausted by the anionic character of the fiber, but is not substantially in excess of the amount capable of being exhausted in or on the fiber. That is to say,
the cationic agent, which is normally active to coagulate subsequently added resin in aqueous medium, is included in the slurry in an amount which will be substantially completely exhausted by the fibers as indicated by the absence of the agent in the aqueous medium and not in such an excess amount as will render the presence of free agent in the aqueous medium detectable by titration with brom-pheno1 blue, whereby coagulation of the resin in aqueous medium is substantially eliminated. As will be appreciated, it is desired to limit the amount of free or excess cationic agent as much as possible in order to substantially eliminate or reduce the possibility of coagulation in the aqueous phase of the subsequently added resin. It is recognized that in practical commercial operation traces of free agent as well as slight excesses of the free agent will accidentally be present in many cases and therefore the present invention comprehends such cases, namely where such excess of free agent is not sufficient to cause objectionable coagulation of the resin in the aqueous phase. Upon the addition of the cationic active material, the slurry is agitated to produce the absorption of the same in or on the fibers.

Thereafter, there is added to the slurry containing the fibers which have been charged by the activity of the cationic substances and which may be said to now have acquired a positive charge, an amount of water soluble polyvalent metal salt which will be exhausted or absorbed in or on the charged fibers but which will not be in amount substantially greater than will be completely exhausted by the cationic active agent treated fibers in order to avoid coagulation of the subsequently applied coating material. That is to say, the polyvalent metal salt is normally a coagulant for the subsequently added resin in the absence of the aforesaid treatment with cationic active agent. If both an excess of free cationic agent and an excess of the free metal salt are present in the slurry, the condition will be aggravated in that there will be precipitation in the aqueous phase of both the metal salt and the agent and such precipitation will carry down with it the resin particles and thereby remove them from effective use. Therefore, such salt is added to the slurry containing the cationic fibers in amount which will be completely exhausted by such fibers as indicated by the absence of the salt in the aqueous medium and not in such an excess amount as will render the presence of the free salt in the aqueous medium detectable by potentiometric titration. Of course, in practical commercial operation, slight excesses or traces of the free metallic salt may be accidentally present in the aqueous medium of the slurry, and therefore the present invention comprehends such cases, namely where such excess of free agent is not sufficient to cause objectionable coagulation of the resin in the aqueous phase.

We have found that highly effective results are obtained by treating the fibers with a cationic active agent prepared by reacting a member of the group consisting of alkyl sulphates, phosphates (preferably the tripolyphosphate) and sodium with an organic unsaturated compound made by condensing an alkylene polyamine with an acid selected from the group consisting of fatty acids containing 6 to 20 carbon atoms, monohydroxy substituted fatty acids containing 6 to 20 carbon atoms, dicarboxylic acids containing 4 to 10 carbon atoms and tall oil which latter is a product containing a mixture of fatty acids and rosin acids recovered from the black liquor derived from the treatment of wood fiber by the kraft process. In the polyamine-acid reaction, the resultant soap is dehydrated and the dehydrated amide which is an aliphatic, alkylene polyamide is then alkylated to produce a dehydrated aliphatic, alkylene polyamide. We have found that the extent of cationic activity was related to amount of water removed during the amiation step. That is, it was found that if the amiation step was not carried to completion, the final alkylated product was not as cationically active as when all the water was removed, because alkylation did not proceed as fast or as completely, unless substantially all water was taken off during the amiation. For instance, it was found that a much stronger cation active compound could be produced by distillation of all of the water from the product during the amiation, thereby giving an anhydrous intermediate which could be ethylated in such a manner that both ethyl groups were bonded during the reaction.

Examples of suitable alkylene polyamines are straight chain alkylene polyamines having the general formula \(H_n(C_2H_4NH)_m\cdot C_2H_5NH\) wherein \(n\) is 1 to 4, such as triethylene tetramine, tetraethylene pentamine, diethylene triamine and polyethylene amines having an approximate or average molecular weight of 1200 to 1800 which are straight chain ethylene amines polymeric to a point at which the ethylene amine grouping is continued, i.e., in straight chain until a molecular weight of 1200 to 1800 is produced. These latter compounds have primary terminal amine groups and secondary internal amine groups and are typified by the above formula. Also, suitable examples are straight chain alkylene polyamines having the formula \(H_n(C_2H_4NH)_m\cdot C_2H_5NH\) wherein \(n\) is 1 or 3, such as dipropylene triamine and tripropylene triamine. Suitable examples of alkylene polyamines are derived from 1,3-butan diamine, being a polyamine hydrocarbon with 4 carbon atoms between nitrogen atoms plus 1 extra amino group on each group of 4 carbon atoms and having an approximate or average molecular weight of 185 and showing an average of 2.6 nitrogen atoms per mol of polymer, the amino groups being divided about one-half primary and one-half secondary, 20% of the compound boiling below 210°C and 70% boiling below 280°C. In carrying out the invention one or a mixture of any of the foregoing polyamines may be employed.

Suitable fatty acids, are the fatty acids of cocosnut oil, and, in fact, any fatty acid or mixture of fatty acids, saturated or unsaturated, having from 6 to 20 carbon atoms in the chain, e.g., capric acid, arachidic acid, and oleic, stearic, palmitic, myristic, lauric, hydroxv substituted fatty acids, linoleic, linolenic, and mixed acids resulting from the splitting of the glycerides of the commonly available fats and oils, such as cocosnut, castor, cottonseed, soya, and tallow. Also, hydroxy substituted fatty acids, such as ricinoleic acid may be used. In addition to the straight chain fatty acids, dicarboxylic saturated and unsaturated acids having 4 to 10 carbon atoms may be used, notably sebacic acid, adipic acid, maleic acid, succinic acid, and suberic acid. Also, tall oil, as above mentioned, may be employed. In carrying out the invention, one or a
mixture of any of the aforesaid acids may be used.

For the purposes of alkylation, dimethyl, diethyl or dipropyl sulphate or the mono-, di- or tri-
methyl, ethyl and propyl phosphates may be used; also alkyl halides, such as methyl, ethyl or propyl chlorides, or bromides, namely the mono and dichlorides and bromides may be employed. Mixtures of the alkylation agents may be used.

We have discovered that a further satisfactory cationic active agent is prepared by alkylation of the product obtained when any of the amidation products formed herein are reacted with 1 mol of urea to an amount of urea which is 1 mol less than the total number of nitrogen atoms present in the alkylene polyamine used in forming the amidation product. The reaction is carried out by reacting one or a mixture of the amidics and the urea at temperatures not in excess of 190° C. and not less than 75° C. in an open or closed system.

We have found that when the fibers are first treated with a cationic coupling agent prepared by the reactions above-described subsequent coating of the base is achieved in a manner to produce a marked increase in the amount of coating material picked up by the base per unit area thereof, and, moreover, the adherence and abrasion resistance of the coating or impregnant is substantially enhanced.

Many water soluble polyvalent metal salts may be utilized, among which are paper-makers alum as well as di-, tri- and tetra-valent metallic salts of chloride, sulfate and phosphate, in combination with barium, calcium, magnesium, aluminum, chromium, ferric iron, copper, lead, tin, gold, silver and Platinum. The slurry to which has been added the soluble polyvalent salt is agitated to effect the same upon the fibers which have been treated prior to the introduction of the salt with a cationic active agent as above described.

There is now incorporated with the slurry any coating material such as synthetic and natural resins, natural and chemically produced rubbers, pigments, color emulsions and dispersions. Resins useful in this process are negatively charged aqueous emulsions, suspensions, dispersions and solutions such as: phenol formaldehyde, resorcinol formaldehyde, alkyd, urea formaldehyde, acryllic, polystyrene, butadiene styrene, polyethylene, polyisobutylene, natural rubber latices, hycar, neoprene, CR-S type synthetic rubbers, thikol, protein formaldehyde, polyvinyl chloride, polyvinyl acetate, polynvinyl butyral, styrene maleic anhydride polymethacrylate, cumar, drying oils such as tung, linseed and oiticica oils, soya bean oil, allyl polymers such as di-allyl phthalate, resin, indene, cumarone indene, ketone aldehyde, asphalt, melamine, melamine formaldehyde vinylidine chloride, inoert pigment suspensions and dispersions, resin-pigment dispersions, copolymers of vinyl chloride-vinyl acetate, copolymer of vinylidene chloride-vinyl chloride, nylon, cellulose acetate, cellulose acetate butyrate, acrylonitrile, polymerized chlorobutadiene, and numerous others. It is to be understood that these resins may or may not be plasticized with the usual plasticizers normally combined with the individual resins.

The coating material will be in aqueous medium, namely, in solution, dispersion or emulsion, and liquid or solid particles may be suspended in the outer or continuous aqueous phase according to the nature of the coating material. Mixtures of the coating materials may be used.

Such anionic coating materials when introduced into the slurry prepared as above-described and agitated, have been found to uniformly penetrate and adhere to the fibers. In the manufacture of paper products it is preferable to introduce the coating material into the head box or boxes or pulp vats of the paper-making machine, although it may be introduced in any of the previous stages of the paper-making operations subsequent to the exhaustion of the metallic ion.

The slurry treated as above-described and containing the coating material may be fabricated upon the cylinder or Fourdriner machine, Yankee or Harper machines. It is observed that there is no sticking of the fibers or of the coating material to the wires or screens of such apparatus.

Moreover, an examination of the white water from the paper machine discloses substantially complete absence of any of the incorporated substances so that the element of waste which has heretofore been a considerable item in the production of impregnated paper on paper-making machinery is substantially overcome. The foregoing results which are quite unexpected are due to the operations involved in the invention being critical in that the steps must be performed in the sequence indicated up to the time of formation of the web on the machine.

Thereafter, the web is carried from the wire or screen and treated as is customary, e.g., is traveled over the usual drying drums or cans then calendared if desired, and the coating material, if necessary, may be cured by heat, pressure or both, as part of the continuous paper-making operation or by a subsequent or independent operation.

When it is desired to produce a laminated paper, for example, in the case of the Fourdriner machine, a suitable number of beater processes are provided, delivering respectively to head boxes suitably arranged with respect to the screen of the Fourdriner, so as to deposit the layers of pulp of different consistency and containing either different resins or different amounts of resins respectively to form a single integral laminated Fourdriner sheet. Like procedure can be followed in the case of a cylinder machine by varying the treatment of the pulp and the amounts and kinds of resins included in the respective cylinder vats. With respect to either the Fourdriner made paper or the cylinder made paper, certain of the pulps may be colored either by the introduction of a pigment or suitable dye and, in fact, a surface coating may be applied to the web of either type of paper, for instance, as the last step in the operation before drying or such coating may be applied to the surface of the dry web before or after drying or prior to or subsequent to calendaring or curing.

Since the character of the fibres will frequently vary, and also the cationic agents and metal salts which are utilized, it is not possible to strictly set forth the specific amounts of the particular treating substances which are incorporated in the slurry. However, for any specific run, it is a simple matter for an operator to examine and test the slurry and thereby determine within rather narrow limits the amount of cationic agent which it is necessary to incorporate in the slurry, and the amount of polyvalent metal salt which it is necessary to incorporate thereafter in the slurry to obtain the best result, and particularly
it is easily determinable to limit the amount of such substances which can be incorporated without producing undue coagulation of the coating material or sticking to the apparatus which results from such coagulation. These requirements are critical, as will be appreciated, as well as the specific sequence of steps as was indicated above.

One of the important advantages of the present invention which has been observed by practical operation is attributed to the penetration of the fibre by the coating material which, due to the preliminary treatment of the fibre, allows the resin or rubber or mixtures of the same to penetrate the capillaries of the fibre to thereby replace a substantial amount of occluded water. Hence, it is possible to dry a sheet of paper or board made according to this invention much more rapidly than ordinary paper sheets produced on conventional paper machinery and it follows that the paper-making machinery can be utilized to substantially increase the productivity because this is not contingent upon a retarded drying, as is now the case. Moreover, and of substantial advantage, is the fact that the penetration and coating and adherence of the resin material to the short fibres ties these in with the long fibres in such a way that the customary losses of short fibre through the wire or screen is almost entirely precluded. We have also observed that the paper products produced in the manner described are dimensionally stable, i.e., they exhibit less shrinking in the drying operation and are less susceptible to changes in humidity and temperature, and also preserve their flat nature against warping or curling, such as is encountered with ordinary paper.

Another striking advantage of the invention resides in the ability to produce a thicker sheet which is uniformly impregnated with the coating material. Heretofore, when either a laminated web or relatively thick sheet or board was necessary, the laminations had to be made relatively thicker in order to assure that they would be properly saturated with resin as is common practice before laminating. With the present invention, however, laminating may be eliminated where thick board is to be produced. Where laminating is to be employed, less layers will be used because relatively thicker layers can be formed for each sheet to be laminated. Where it is desired to adhere two or more layers together, it is found that sheets produced according to this invention, whether of a thick or relatively thin character can be readily united by heat and pressure since the selected resin or rubber material may be fused sufficiently to produce an integral structure.

While the resins may be introduced to the slurry in the beater, or at any point prior to the introduction of the slurry upon the screen, we find it preferable to add the resins to the head box or head boxes of the Fourdrinier machine or to the vats of the cylinder machine because at such point, the stock is in its optimum paper-forming condition.

The pulp or stock to which the resin has been added, whether in the head boxes or cylinder vats or at some point prior thereto, when examined under the microscope, shows that the resin has been uniformly adsorbed and absorbed by the fibres, as distinguished from being disposed in the interstitial spaces between the fibres. In other words, the mechanical lodgement of the resin in the fibrous mass which has been the customary result, is substantially eliminated by this invention, and it is due to this fact that the stock exhibits a marked and highly desirable freeness. Incidentally, there is no tendency of the stock to penetrate beneath the wire or to stick to the same.

When a web is laid down from such stock, the white water is substantially free of resin particles, cationic agent and metallic salt or short fibre and the web, upon examination, discloses that the resin remains adsorbed and adsorbed upon the fibres so that the subsequent sheet will be distinguished from the customary resin treated webs by the substantial absence of resin which is held mechanically in the interstitial structure of the sheet.

The sheet or board produced by the felting operation can be readily distinguished from the products of conventional processes by reason of the fact that the resin is absorbed and adsorbed uniformly upon the fibres throughout the thickness of the web. This is in contrast to conventional webs wherein there are interstitial accumulations of resin and agglomerated masses of coagulated resin, all of which are highly objectionable.

Of the various types of cellulosic fibres which may be satisfactorily formed into webs in accordance with this invention, to mention a few are wood pulp, cotton, cotton linters, reprocessed rag fibres, regenerated cellulose, bast fibres, jute, flax, hemp, straw, grasses, rye, wheat, oats, barley, rice, ramie, sisal and corn stalk fibres.

While the invention lends itself particularly to the manufacture of paper-like webs or boards, whether of single layer or laminated structure, it can also be used for the preparation of molded products by utilizing the wet web formed on the web-forming instrumentality, in accordance with conventional practice. The wet web is identified not only by characteristics above set forth, but also by possessing a maximum of plasticity.

With respect to the treatment of the wet web for the formation of final structures, the drying, the heat and pressure steps, and the curing and setting of the resin are all conducted in accordance with conventional procedure which forms no part of this invention.

Example 1
(Forming the cationic agent)

A suitable cationic coupling agent is prepared by mixing 1 mol of the mixed fatty acids of coconuot oil with 1 mol of diethylene triamine, and reacting the same in a closed still at about 125°C. until at least 1 mol water has been distilled over. Temperatures from 120°C. to 200°C. are suitable. With vacuum, lower temperatures are possible. The dehydrated resultant product was reacted with 1 mol of dimethyl sulphate at 100°C. to 200°C., for instance, at a temperature of about 150°C. until maximum cationic activity was obtained. This required approximately one hour after the initial temperature rise occasioned by the violent reaction of the dimethyl sulphate with the dehydrated amine. The product was then diluted with water to about 40% active ingredient yielding a water soluble, light yellow, viscous liquid which was successfully used in the following examples on a fibrous base and a fabric base. The dilution, of course, may be carried out to any desired concentration and is done primarily to facilitate ease in handling.

Instead of the fatty acids from coconuot oil,
any fatty acid or mixture of fatty acids, saturated or unsaturated, having from 6 to 20 carbon atoms in the chain, as indicated above, may be employed. Instead of the diethylene triamine any of the polyamines mentioned herein or mixtures thereof may be used. The amidation product may be condensed with urea as above-described and then alkylated. Also mixtures of the amidation products may be employed.

Example 2

A suitable cationic active material has been prepared as in Example 1 above except that after the amidation step, 2 mols of the amine are reacted in a closed system between 110° C. and 190° C. with 1 mol of urea, yielding a product of the general formula

\[
\begin{array}{c}
O \\
H \\
R-C-\text{NOCHNHCH}_2 \text{CH}_2 \\
C=O \\
O \\
H \\
R-\text{NOCHNHCH}_2 \text{CH}_2 \\
O \\
H \\
H
\end{array}
\]

where R is an aliphatic straight chain and derived from the fatty acids.

One mol of the above product is then alkylated with 1 mol of diethyl sulphate at 130° C. to 200° C. until maximum cation activity is obtained. The product may then be cut to 40% active ingredients with water yielding a water soluble viscous mass.

It is to be understood, of course, that any of the polyamines mentioned herein and mixtures thereof, any of the fatty acids mentioned herein and mixtures thereof, any of the amidation agents and mixtures thereof may be employed in the foregoing examples. Likewise, the amidation products can be condensed with urea as above described and then alkylated.

Example 3

A suitable cationic coupling agent is prepared by mixing 1 mol of sebacic acid with 1 mol of tetraethylenepentamine and reacting in a closed still at temperatures from 120° C. to 200° C. for instance 125° C. until at least 1 mol of water had been distilled over. The resultant dehydrated product was reacted with 1 mol of diethyl sulphate at a temperature of about 130° C. until maximum cation activity was obtained. This ethylation reaction may be carried out between 120° C. and 200° C. However, at 180° C. the reaction required approximately one hour after the initial temperature rise occasioned by the violent reaction of diethyl sulphate with the dehydrated amide. The product was then diluted with water to about 40% active ingredients yielding a water-soluble viscous liquid which was successfully used in the bonding of synthetic or natural resin to a negatively charged fibrous or fabric base. The dilution of this product may be carried out to any desired concentration, and is done primarily to facilitate ease in handling.

Example 4

The procedure described in Example 3 is em-
the resin. The beater stock was then treated with 7% alum based on the weight of the bone-dry fibre. A sample of the beater stock after this treatment was weighed so as to have an equivalent of 10 grams of bone-dry fibre in the slurry. Small aliquots of 10% polyni vinyl chloride emulsion was added to this sample of pulp with agitation, with 10 to 15 seconds elapsed time between additions, allowing for pick-up of the resin. It was found that 475% of the resin based on the weight of the bone-dry fibre could be added to the slurry before the white water started to show traces of uncombined free resin in the white water. This indicated that a 475% addition could be safely made. However, it was desired to make a sheet of 50% pulp and 50% resin. It was then considered safe practice to add 100% (solids content) of polyni vinyl chloride to the stock based on the weight of the bone-dry fibre just prior to flowing the slurry on the wire or screen, i.e., to the head box of the Fourdriner. The character of the web formation on the wire showed an excellent freeness of stock and there was no sticking of particles of fibre or resin to the wire as the web was traveled from that point to the driers. Likewise, there was no penetration of the wire by the stock and no sticking of the web to the felts or drying drums.

Example 6

Similar operations to Example 5 were made wherein GH-S type latex and also hyacryl poly styrene, and butadiene styrene latexes, isobutylene, urea formaldehyde and neoprene were used as well as phenol formaldehyde resin in the amounts of 100% resin solids based on the weight of the bone-dry fibre. In each case there was excellent freeness of the pulp at the wire and good formation of a sheet which had no coagulation or sticking at the wire. It is an accepted fact that where there is coagulation, as has been the results of previous processes, there will be sticking of particles on the wire.

The foregoing examples are merely illustrative since it will be understood that various of the fibres and mixtures thereof may be utilized with various of the alkylated amiation products and mixtures thereof. Likewise, various of the metallic salts and mixtures thereof may be employed. In connection, and as explained above, a multiplicity of beaters may be employed containing different pulps and having different consistencies for feeding to the wire, and there may be mixed with such pulps various of the resins and mixtures thereof. The number of combinations which may be so made is infinite. The alkylated amiation products described herein have produced most unusual results in combination with the steps of the operation in the critical sequence recited. While for perfect results the quantities of cationic agent and metallic salt should be held within the limits indicated above, it is realized that exact perfection cannot be maintained in large continuous operations for which the invention is useful in papermaking and board plants, and, therefore, slight tolerances from the strict limits recited are acceptable. However, any substantial departure from such limits must be avoided in the interest of preventing coagulation of the resin and the resultant formation ofummy deposits on the paper-making wire or screen and the production of sheets which lack a uniform structure and resistance to splitting.

We claim:

1. The method of incorporating resinous materials with negatively charged cellulosic fibres in aqueous suspension which comprises rendering the fibres cationically active by mixing them with an aqueous solution of a cationic active agent prepared by reacting 1 to 2 mols of a member of the group consisting of alkyl sulphates, phosphates and halides having 1 to 3 carbon atoms in an alkyl group with a dehydrated amiation product made by condensing in the presence of heat 1 to 5 mols of a compound selected from the group consisting of straight chain alkylene polymethylenes having the general formula

\[ \text{H}_n\text{(CH}_2\text{NH})_x\text{(CH}_2\text{NH)}_n\text{H} \]

wherein \( x \) is 1 to 4; the general formula

\[ \text{H}_n\text{(CH}_2\text{NH})_x\text{(CH}_2\text{NH)}_n\text{H} \]

wherein \( x \) is 1 or 2; and an alkylene polyamine derived from 1,3-butanediol, being a poly amino hydrocarbon with 4 carbon atoms between nitrogen atoms plus one extra amino group on each group of 4 carbon atoms having an average molecular weight of 185 and showing an average of 2.6 nitrogen atoms per mol of the amino groups being divided about one-half primary and one-half secondary, 20% of the compound boiling below 210° C. and 70% boiling below 380° C., with 1 to 4 mols of an acid selected from the group consisting of tall oil acids, fatty acids containing 6 to 20 carbon atoms, monohydroxy substituted fatty acids containing 6 to 20 carbon atoms and dicarboxylic acids containing 4 to 10 carbon atoms until 1 to 10 mols of water are distilled off, such agent being added in an amount which will be completely exhausted by the fibres as indicated by the absence of free agent in the aqueous medium and not in such an excess amount as will render the presence of free agent in the aqueous medium detectable by titration with Brom-Phenol Blue, adding to the fibres following treatment with the cationic agent and mixing alum with the aqueous suspension, said alum being added in amount which will be completely exhausted by the cationic fibres as indicated by the absence of the alum in the aqueous medium and not in such an excess amount as will render the presence of free alum in the aqueous medium detectable by potentiometric titration, and thereafter mixing a negatively charged resin in aqueous medium with said fibres in aqueous medium, whereby the resin is deposited in and upon the fibres.

2. The method according to claim 1 wherein, before alkylation, the amiation product, which is the reaction product of the polyaniline and the acid, is reacted in the proportion of 2 mols of amiation product to 1 mol of urea to a quantity of urea which is 1 less mol of urea than there are nitrogen atoms present in the alkylene polyamine used in forming the amiation reaction product, the reaction between the amiation product and the urea being carried out at temperatures not in excess of 150° C. and not less than 78° C.

3. The method according to claim 1 comprising feeding the resin-carrying fibres in aqueous medium to a web-forming instrumentality and forming a web therefrom.

4. The method according to claim 1 comprising adding and mixing the resin in aqueous medium with the fibres in aqueous medium at a point adjacent a web-forming instrumentality, supplying the resin-carrying fibres in aqueous medium to a web-forming instrumentality.
medium to the web-forming instrumentality, and forming a web.

5. The method according to claim 1 wherein the polyamine has the general formula

\[ \text{H}_2\text{N}((\text{C}_2\text{H}_4\text{NH})_2 \cdot \text{C}_6\text{H}_5\text{NH}_2 \]

wherein \( x \) is 1 to 41.

6. The method according to claim 1 wherein the polyamine has the general formula

\[ \text{H}_2\text{N}((\text{C}_2\text{H}_4\text{NH})_2 \cdot \text{C}_6\text{H}_5\text{NH}_2 \]

wherein \( x \) is 1 or 2.

7. The method according to claim 1 wherein the alkylene polyamine is derived from 1,3-butane diamine, being a polyamine hydrocarbon with 4 carbon atoms between nitrogen atoms plus one extra amino group on each group of 4 carbon atoms, having an average molecular weight of 185 and showing an average of 2.6 nitrogen atoms per mol; the amino groups being divided about one-half primary and one-half secondary, 20% of the compound boiling below 210°C and 70% boiling below 230°C.

8. The method according to claim 1 wherein the polyamine is tetraethylene pentamine.

9. The method according to claim 1 wherein the polyamine is diethylene triamine.

10. The method according to claim 1 wherein the polyamine is triethylene tetramine.

11. The method according to claim 1 wherein the fatty acid is a mixture of coconut oil fatty acids.

12. The method according to claim 1 wherein the fatty acid is tallow oil acids.

13. The method according to claim 1 wherein the dicarboxylic acid is sebacic acid.

14. The method according to claim 1 wherein the said acid, polyamine and alkylating member are used in equi-molecular proportions and the condensing is carried on until 1 mol of water is distilled off.

15. The method according to claim 1 wherein the said acid, polyamine and alkylating member are used in equi-molecular proportions and the condensing is carried on until 1 mol of water is distilled off and wherein the fatty acid is a mixture of coconut oil fatty acids, the polyamine is tetraethylene pentamine and the alkylating member is diethyl sulphate.

References Cited in the file of this patent

UNITED STATES PATENTS

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<tr>
<td>2,096,129</td>
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</tr>
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<td>Smith</td>
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</tr>
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<td>2,343,095</td>
<td>Smith</td>
<td>Feb. 29, 1944</td>
</tr>
<tr>
<td>2,388,154</td>
<td>Katzman</td>
<td>Oct. 30, 1945</td>
</tr>
<tr>
<td>2,391,831</td>
<td>Jayne</td>
<td>Dec. 29, 1945</td>
</tr>
<tr>
<td>2,401,027</td>
<td>Tausch</td>
<td>May 28, 1948</td>
</tr>
<tr>
<td>2,407,376</td>
<td>Maxwell</td>
<td>Sept. 10, 1946</td>
</tr>
<tr>
<td>2,426,780</td>
<td>Plk</td>
<td>Sept. 2, 1947</td>
</tr>
<tr>
<td>2,468,080</td>
<td>Latham et al.</td>
<td>Apr. 26, 1949</td>
</tr>
<tr>
<td>2,497,859</td>
<td>Sherman</td>
<td>Nov. 15, 1949</td>
</tr>
<tr>
<td>2,488,515</td>
<td>Sherman et al.</td>
<td>Nov. 15, 1949</td>
</tr>
<tr>
<td>2,492,702</td>
<td>Neubert et al.</td>
<td>Dec. 27, 1949</td>
</tr>
</tbody>
</table>

OTHER REFERENCES