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APPLICATION OF DISPERSED COATING MATERIALS TO CELLULOSIC FIBERS

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This invention relates to the application of coating or impregnating materials to fibrous cellulosic material, to coated or impregnated cellulosic fibers obtained thereby, and to the manufacture of other articles from the coated or impregnated fibers. More particularly, the invention relates to the incorporation of dispersions or emulsions of water-insoluble coating or impregnating materials such as resins, precipitated or insoluble sizes, elastomers, waxes, pitches, bitumens, oils, etc. into fibrous cellulosic material such as paper stock, cotton, and the like followed if desired by forming the resulting pretreated cellulosic material into fibrous felted sheets or articles such as paper, paper board, moulded or premoulded cellulosic articles and the like. The invention includes processes for the manufacture of new types of paper, paper board, pulp and pulp preforms as well as a wide variety of novel products obtained therefrom, either directly or by subsequent treatments such as shredding, impregnating, cold pressing, hot pressing, heating, calendering, hot calendering and the like.

Heretofore the principal methods of incorporating resins, waxes, waterproofing and greaseproofing agents, binding agents and the like into a sheet of pulp or paper have been by impregnation of the formed sheet or object by a water solution, organic solvent solution or dispersion of the material to be incorporated or by addition of the impregnating agent to the pulp-water slurry, called slush stock or paper stock, either as a substantially water-insoluble dry powdered material or as a precipitate from a water solution, solvent solution, or dispersion or emulsion of the impregnating material. Thus, for example, it is common practice to add fillers such as clay and sizing materials such as rosin soap, rosin or wax emulsions or dispersions, latices, asphalt emulsions and the like to slush stock in the beater, stock chest or at any other point in the stock system prior to sheet formation, preceded or followed by the addition of alum. By this procedure the sizing materials are precipitated and the resulting flocs are entangled or mixed with the fibrous paper stock and are carried into the finished paper.

This procedure works fairly well in those cases where only small amounts of certain materials are added to the paper, such as amounts on the order of 0.5-5% on the weight of the fiber. However, serious operating difficulties are frequently encountered when attempts are made to incorporate larger quantities of impregnating agents

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by these methods. Some or all of the following difficulties are frequently encountered.

1. The resinous material is agglomerated in balls or lumps instead of forming flocs of small particle size. This may cause the sheet to stick to the presses, driers, felts and calenders when the impregnated pulp is run out on a papermaking machine.

2. Coverage of the individual fibers may be poor.

3. Distribution of the resin in the sheet may be non-uniform, resulting in a mottled appearance of the sheet and causing non-uniform ink reception.

4. Sheet formation is often harmed.

5. Precipitation of the resin is frequently incomplete, and much of the resinous impregnating material is lost in the white water.

6. Agglomerates of the resin, together with unprecipitated resin, tend to deposit as sticky aggregates in pipe lines, tanks, and various other portions of the papermaking equipment.

Some of these difficulties, such as the appearance of rosin spots and lumps of agglomerated material are frequently encountered in paper mills even when amounts as small as 0.25-3% of certain types of rosin and wax emulsions are added.

The present invention has as a principal object an improved method for the incorporation of impregnating agents into fibrous cellulosic material in such a manner that many of the difficulties enumerated above are avoided. In accordance with preferred embodiments of the invention, this is accomplished by obtaining a more uniform and complete coating or impregnation of the cellulosic fibers with the impregnating agent prior to the felting or forming step. A second important object is to provide a process for the incorporation of a wide variety of impregnating agents into or upon fibrous cellulosic material in such a manner that these added materials do not seriously interfere with the normal method of production of paper pulp sheets, pulp preforms and the like on standard papermaking equipment, even when large quantities of impregnating materials are used. A further object is to eliminate many of the difficulties ordinarily encountered in the coagulation of resinous dispersions by inorganic precipitating agents such as alum, including difficulties arising through non-uniform coverage of the pulp fibers, formation of sticky aggregates of the precipitated material, and extremely slow drainage of water from

agglomerated resin-fiber masses on the sheet-forming wire or screen.

Further objects of the invention involve the formation, on standard papermaking or pulp-forming or preforming equipment, of easily handled sheets, boards and preforms containing new combinations of fibers, or fibers and fillers, with certain special resinous impregnating agents that have not heretofore been incorporated successfully by slush stock treatment. Thus, for example, certain special thermosetting resins or condensates such as urea-formaldehyde resins, phenol-formaldehyde resins, alkyd resins and the like may be incorporated into paper stock in the quantities necessary for premoulding and moulding processes. Similarly, a wide variety of thermoplastic resins, elastomers and the like may be incorporated in the large quantities necessary for laminating and moulding processes.

A wide variety of organic binders, sizing agents, oils, waxes, pitches, gums and natural resins may also be incorporated. Various combinations of any two or more of these resins may likewise be incorporated if desired. By applying the principles of this invention, resin-impregnated paper or paper board having superior properties can be prepared, as well as new types of products made from the treated paper or pulp by such conventional operations as laminating, moulding, pressing, calendering, extruding and the like. Instead of forming the treated pulps or fibers, they can be shredded, chopped or ground to produce new types of insulating agents, moulding powders, fillers for standard moulding or casting resins, and the like.

The present invention is based on the discovery of an unusual type of flocculation and deposition that is brought about by the action of cationic alkylenepolyamine-halohydrin resins in an aqueous system containing fibrous cellulosic material of the type of paper pulp suspended therein together with an aqueous dispersion of water-insoluble coating or impregnating agents. It has been found that in such a system the cationic alkylenepolyamine-halohydrin resin causes a controlled flocculation such that particles of the impregnating agent are uniformly coated upon or impregnated into the cellulose fibers. When dispersed or deflocculated water-insoluble impregnating or coating agents are applied in this manner the cellulosic fibers retain their property of felting or forming into shaped or sheeted articles despite the presence of large quantities of the impregnating agent, which in some cases may even be greater than the weight of the cellulosic fibers themselves. Moreover, when the proper quantities of cationic alkylenepolyamine-halohydrin resin are applied in the manner hereinafter described a high degree of retention of the flocculated material by the cellulose fibers is obtained, and losses of organic material in the white water system are largely avoided.

The process of the invention therefore comprises as an essential feature the flocculation of an aqueous dispersion of an impregnating agent in the presence of fibrous cellulosic material suspended in the aqueous medium by the action of a cationic alkylenepolyamine-halohydrin resin. The distinctive type of flocculation that is obtained when an aqueous solution of this type of resin is added to an aqueous dispersion such, for example, as an emulsion-polymerized polystyrene dispersion will be described and illustrated hereinafter in greater detail. The invention in its broader aspects includes any process wherein this

flocculating action is used for the deposition or incorporation of an impregnating agent into fibrous cellulosic material.

In addition to the foregoing, one of the most important features of the invention is the discovery that the distinctive flocculating action of the cationic alkylenepolyamine-halohydrin resin continues, and is in many cases actually enhanced, after the cationic resin has been adsorbed on the fibrous cellulosic material. The importance of this discovery resides in the fact that the cationic resin, being distributed uniformly over and through the cellulosic fibers, causes a uniform deposition and retention of the impregnating agent on the fibers after it has been flocculated. Large quantities of any desired impregnating agent are therefore deposited on fibers of cellulosic materials such as paper stock while retaining the felting properties of the fibers, so that after impregnation they can still be felted together and formed into sheeted or moulded products by conventional wet-moulding or papermaking procedures.

Although the invention is not dependent on any particular theory of operation, the following is offered as the most probable explanation of the unusual type of flocculation and retention that is obtained. As is noted above, definite quantities of the cationic polyamine-halohydrin resin are adsorbed upon and retained by the cellulosic fibers when the cationic resin solution is added to an aqueous suspension thereof. As a result of this treatment, the fiber-resin entity becomes positively charged, as contrasted with the negative charge usually associated with cellulose fibers. The resulting positively charged, resin-treated fibers in aqueous suspension exert an appreciable flocculating action on emulsions or dispersions of water-insoluble organic materials, and this is particularly evident when the emulsified or dispersed impregnating material carries a negative charge as when an anionic dispersing agent is employed in its preparation. The result is that after addition of the emulsion or dispersion of the impregnating agent to the aqueous suspension of resin-treated cellulosic pulp, the dispersed particles are attracted to and flocculated on the positively charged fibers forming a layer or coating upon and around the fibers and permitting the formation of a mat of the coated fibers on a screen or paper machine wire, with substantial retention of both the fibers and the coagulated particles of the non-fibrous dispersion.

When the aqueous suspension of cellulosic material is pretreated with a controlled excess of the cationic polyamine-halohydrin resin, over and above that required to impart a positive charge on the cellulose fibers, the unadsorbed positively charged polyamine-halohydrin resin also possesses a strong flocculating action. Therefore when an emulsion or dispersion of an organic impregnating agent is added, two simultaneous flocculating actions occur. Part of the dispersed non-fibrous particles of impregnating agent are attracted to and deposited on the positively charged fibers, forming a substantially uniform coating over the entire fiber surface. Simultaneously, the remainder of the emulsified or dispersed particles are coagulated into small flocs or agglomerates containing in intimate admixture the polyamine-halohydrin resin and particles of the added emulsion or dispersion. These flocs or aggregates of combined resins, by reasons of their finely divided condition, readily

coat or entangle with the fibrous portion of the mixture and offer little resistance to the drainage of the water during felting and forming of a sheet or mass of the pulp on a screen or wire. As a result of these combined flocculations it is possible, by proper control of the amount of added polyamine-halohydrin resin and other factors, to obtain complete or nearly complete retention of both the cationic resin and almost any desired proportion of organic impregnating agents.

Although the foregoing is regarded as the most probable explanation of the phenomena involved, the process of the invention is not necessarily limited thereto. On the contrary, it is possible that other factors may play an important part in the flocculation of the dispersed impregnating agents. Thus, for example, both the cellulose fibers and the alkylenepolyamine-halohydrin resin attached thereto, as well as the excess polyamine resin remaining in aqueous suspension, undoubtedly present enormous surfaces upon which the molecules of various emulsifying agents can be adsorbed from water solution. It is therefore quite possible that the polyamine resin-coated fibers, as well as the polyamine-halohydrin resin itself, may adsorb appreciable quantities of emulsifying or emulsion-stabilizing agents associated with a third component added to the system, and thereby contribute to the flocculation of the particles of the third component and their agglomeration on the fibers. This mechanism may explain why materials dispersed by means of non-ionic or in some cases even by cationic dispersing or emulsifying agents are often retained with cellulose fibers by means of the cationic alkylenepolyamine-halohydrin resin solution.

The flocculating agents used in practicing our invention, and which are designated for convenience as "polyamine-halohydrin resins" are reaction products of polyamines with polyfunctional halohydrins such as a dihalohydrin, e. g. alpha-dichlorohydrin, dibromohydrin or di-iodohydrin or any of the corresponding monohalohydrins containing a second radical or group capable of reacting or promoting reaction with a polyamine such as epichlorohydrin, epibromohydrin, epi-iodohydrin, di-epi-iodohydrin and the like. Although arylenediamines such as p-phenylenediamine may be used in preparing these resins the preferred compounds are alkylenepolyamines, since these form colorless resins with halohydrins whereas the corresponding resinous condensation products of the arylenepolyamines are likely to be highly colored.

The alkylenepolyamines used in preparing the resins employed in practicing our invention are well-known compounds corresponding to the formula $H_2N(C_nH_{2n}.HN)_xH$ in which x is one or more. Typical amines of this class are the alkylenediamines such as ethylenediamine and 1,3-propylenediamine and polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and the corresponding polypropylenepolyamines and polybutylenepolyamines. The halohydrins are derivatives of glycerol in which one terminal hydroxy group is substituted by a halogen atom; i. e., by chlorine, fluorine, bromine and the like. We have found that the presence of a terminal halogen atom in these reagents imparts cationic properties to the resins which they form by reaction with alkylenepolyamines, and this is probably the reason why these resins are substantive to cellulose fibers.

The condensation between the polyamine and

the halohydrin is believed to take place in two stages, the first being a simple linear condensation and the second a polymerization or self-alkylation reaction. We have found, however, that resinous products suitable for use as flocculating agents in the process of the present invention are obtained without the necessity of obtaining a thermosetting resin by this reaction. Thus, for example, excellent results are obtained with condensation products of equimolecular quantities of polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine and epichlorohydrin or dichlorohydrin, even though the condensation at this molecular ratio yields resins which are not thermosetting. On the other hand, the condensation product of two mols of epichlorohydrin or dichlorohydrin with one mol of a polyalkylenepolyamine such as tetraethylenepentamine is thermosetting in character, and can be used where a thermosetting resin is desired. Larger proportions of the halohydrin can be and frequently are employed where a thermosetting resin having a greater speed of cure is desired, the optimum being between about 2:1 and 3:1. When more than four mols of the polyfunctional halohydrin are used for each mol of tetraethylenepentamine or similar polyalkylenepolyamine the resin is thermosetting but the syrups are less stable in character and must be manufactured and stored at concentrations of less than 10% to avoid premature gelation.

The cationic polyamine resins used in practicing the present invention are therefore prepared by reacting one mol of a polyamine, and preferably an alkylenepolyamine such as ethylenediamine or a polyalkylenepolyamine such as diethylenetriamine or tetraethylenepentamine with one or more mols, preferably 1-3 mols, of a polyfunctional halohydrin. This reaction is preferably carried out at temperatures below the boiling point of the mixture, usually not substantially higher than 60°-70° C., in order to permit the use of relatively concentrated solutions while obtaining the resin in a hydrophilic or water-dilutable condition. Usually the halohydrin is added slowly to the polyamine, which is preferably dissolved in water or a water-miscible solvent, at a rate such that the reaction temperature is maintained at about 50°-55° C.

When a thermosetting resin is desired the reaction product, after the initial exothermic reaction, may be maintained at 60°-70° C. until an increase in viscosity is noted, indicating that the second stage of the resin-forming reaction has set in, after which it is cooled and diluted with water if necessary to form a stable syrup. In some cases, and particularly where a dihalohydrin is being used, sufficient alkali such as sodium hydroxide, sodium or potassium carbonate, or sodium or potassium phosphate may be added before or during the second stage of the reaction to neutralize the syrup by combining with any hydrohalide that is not taken up by the polyamine. This alkali addition also frequently gives improved results when condensing a polyamine of relatively low molecular weight, such as ethylenediamine, diethylenetriamine, or triethylenetetramine with several molecular proportions of a monohalohydrin such as epichlorohydrin in the preparation of a thermosetting resin. If desired the syrup may be subjected to a vacuum distillation after the first stage of the reaction is completed to remove any unreacted epichlorohydrin, dichlorohydrin or other polyfunctional halohydrin.

Any water-insoluble coating or impregnating agent may be applied by the process of the invention in amounts varying from a few per cent up to more than the weight of the fibrous cellulosic material. By "coating or impregnating agent" we mean, of course, a material which will coat or impregnate the cellulosic fibers and improve their value for their intended use. The great majority of coating and impregnating materials used in practicing the invention are organic amorphous or micro-crystalline materials of the type of waxes, gums, resins and the like. The following types of materials of this class are illustrative of the wide variety of impregnating agents that may be applied:

Waxes

Paraffin	Microcrystalline or
Crude scale wax	amorphous petro-
Carnauba wax	leum wax
Montan wax	Chlorinated waxes
Petrolatum	

Bituminous

Asphalt	Bitumens
Tars and pitches	

Rosins

Wood rosin	Acid-treated or poly-
Gum rosin	merized rosin
Heat-treated rosin	Hydrogenated rosin
Disproportionated rosin	Limed rosin
in	Sulfur-treated rosin

Elastomers

Natural latices	Butadiene polymers
Synthetic latices	Copolymers of buta-
Isoprene polymers	diene, isoprene, etc.
Neoprene polymers	with acrylonitrile

Resins—Thermosetting

Phenol-aldehyde resins including particularly the phenol and alkyl-phenol formaldehyde moulding resins

Pine-wood pitch-phenol-formaldehyde resin dispersions (U. S. Patent No. 2,357,091)

Lignin-phenol-formaldehyde resin dispersions (U. S. Patent No. 2,357,090)

Urea-aldehyde resins

Furfural-formaldehyde and furfuryl alcohol-formaldehyde resins

Alkyd resins

Non-cationic melamine-formaldehyde resins

Alkylated or alcohol-reacted urea-formaldehyde resins

Alkylated or alcohol-reacted melamine-formaldehyde resins

Resins—Thermoplastic

Polyvinyl compounds

Polystyrene

Polyacrylates

Polymethacrylates

Polyvinyl esters such as vinyl chlorides and vinyl acetate polymers and copolymers of the two

Polyvinyl acetal

Polyvinyl alcohols

Copolymers of styrene with vinyl chloride, acrylic acid esters, acrylonitrile, etc.

Thermoplastic phenol-formaldehyde resins, including phenol-acetaldehyde and phenol-furfural resins and corresponding resins obtained from cresols and other alkyl phenols

Oil-modified phenol-formaldehyde resins

Esters of rosin with polyhydric alcohols such as glycerine, pentaerythritol, dipentaerythritol, polyallyl alcohols, etc.

Resins from melamine and higher aldehydes

- 5 Polyindene resins
- Coumarone resins
- Vinylacetylene resins
- "Vinsol" resin; i. e. residue from purifying wood rosin
- 10 Halogenated vinylacetylene resins
- Acetyl gums

Any of the above materials, either singly or in admixture, may be applied to fibrous cellulosic materials with the aid of cationic alkylene-polyamine-halohydrin resins by the process of the present invention. The impregnating agent is added to the aqueous stock suspension containing the cellulose fibers as a dispersion in water or aqueous liquid. Depending on the type of impregnating agent, the dispersions may require no added emulsifying or dispersing agents whatsoever, as in the case of natural latices. However, in many cases dispersions of finer particle size and better impregnating properties are obtained with the aid of dispersing agents, and many types of dispersing agents may be used. In general, any anionic or non-ionic dispersing agent may be employed in emulsifying or suspending the impregnating agents in water or other aqueous liquids, and in certain cases the cationic emulsifying agents may also be used. Typical anionic emulsifying agents which have been employed with success are the soaps of aliphatic and cyclo-aliphatic acids such as potassium oleate, potassium naphthenate and the like, amine soaps such as triethanolamine oleate; sulfated aliphatic compounds such as sodium lauryl sulfate and the sulfates of higher secondary alcohols and sulfonated castor oil; sulfonated products such as sodium keryl benzene sulfonate, sodium isopropyl naphthalene sulfonate, esters of sulfo-carboxylic acids such as esters of sodium sulfoacetate, dialkyl sulfosuccinates, disodium monoalkyl sulfosuccinates; amides of sulfo-carboxylic acids such as sodium sulfosuccinamates and the like, sulfonated lignin, etc.

Non-ionic emulsifying agents such as polyhydric alcohol esters and ethers may also be used. Typical compounds of this class are polyethylene glycol-substituted maleic acid esters of the formula



mannitan and sorbitan monoesters of higher fatty acids such as palmitic, stearic and oleic acids and their ethylene oxide condensation products and aryl-alkyl polyether alcohols.

Another class of compounds that may be used either as emulsifying agents or as emulsion stabilizers are the gums and proteins. Thus, for example, gum arabic may be used, as well as soya-bean protein, sodium alginate and the like. Ammonium caseinate is another emulsifying agent that has been used with success.

Ammonium or other water-soluble or water-dispersible salts of alkyd resins of high acid number may also be employed, such as the products obtained by adding sodium hydroxide to condensation products of maleic acid and glycerine, modified phthalic anhydride-glycerine-fatty acid condensation products of high acid number, polyhydric alcohol, esters of terpene-maleic acid condensation products and the like.

In general, therefore, any suitable wetting or

emulsifying agent may be used in practicing the invention.

Any fibrous cellulosic material capable of adsorbing cationic polyamine, halohydrin resin from an aqueous solution thereof may be coated or impregnated by the process of the invention. A wide variety of fibrous cellulosic material used in the preparation of paper, board, moulded resin fillers and the like may be used, such as Kraft pulp, rag pulp, soda, sulfate, ground-wood, sulfite pulp and alpha pulp. Similarly, other forms of fibrous cellulose such as cotton linters, and the like may be employed. These materials may be used alone or in admixture with fibers from other sources, such as jute, hemp, sisal, strings, chopped canvas, asbestos fibers, glass fibers, and other material, either cellulosic or noncellulosic, that may improve the impact resistance, mechanical strength or other properties of the formed or moulded impregnated material. Typical products that may be improved by the process of the invention are waterproof or moisture-vaporproof paper, paper or board containers or cartons for milk, butter, foods, etc., resin-impregnated laminating paper, abrasives composed of resin-impregnated paper coated with abrasive particles, moulded articles, pre-moulded articles, electrical insulators, filter paper, heat-insulating paper, or loose masses of unfelted and unmoulded impregnated cellulose stock used for air filters, dust filters, heat insulation and the like.

The particular procedure whereby the impregnating agent is flocculated and coated on the fibrous cellulosic material may vary somewhat with different impregnating agents, but usually follows the same general plan. The cellulosic material is preferably first suspended in water and may be beaten for shorter or longer periods of time, after which the stock may be brushed out in a Jordan engine or other refining machine if desired. Any desired ratio of cellulosic material to water may be maintained, but we prefer to operate at a stock consistency of about 0.5% to 6%. The cationic alkylene-polyamine-halohydrin resin is then added, preferably in the form of an aqueous dispersion of about 5-15% resin solids, after which the stock suspension is preferably allowed to stand for anywhere from 15 minutes up to 3-4 hours or longer. This period of standing is not a necessary step, since the adsorption of cationic resin by the paper pulp is quite rapid, but the subsequent behavior of the impregnated stock on a papermaking machine is much better when the addition of the impregnating agent is delayed for this period of time. The pH of the stock during the adsorption of the cationic polyamine-halohydrin resin and prior to addition of the impregnating agent should preferably be within the range of about 3-8 since the resin retention is not as good at higher or lower values.

After pretreatment of cellulosic fibers with the cationic alkylene-polyamine-halohydrin resin, the impregnating agent is introduced in the form of an aqueous suspension, preferably of relatively fine particle size. The flocculating action of the cationic polyamine resin is not dependent on the particle size of the added impregnating agent, but a much more uniform coating of the cellulose fibers and better performance on the papermaking machine is obtained when a dispersion of fine particle size is used. Aqueous dispersions having an average particle size of 1-2 microns

or less have given excellent results in practice, and therefore we recommend the addition of the impregnating agent in the form of an aqueous dispersion having at most this particle size. The flocculation of the impregnating agent and its adsorption by the cationic resin-treated cellulose fiber is fairly rapid, and the standing time of the mixture after the impregnating agent has been added makes very little difference in the resin retention. The stock can therefore be formed immediately after the addition of the impregnating agent or after a considerable period of time, as desired. However, a more uniform impregnation of the stock is sometimes obtained when the impregnating dispersion is added slowly to the resin-treated stock instead of adding it all at once. In continuous operation, where the resin dispersion is added continuously to a stream of the treated stock, this effect can be obtained by introducing the resin dispersion simultaneously at several points in the stock-treating system. Also the point of addition can be selected so that the time of contact available for flocculation before sheet formation is adjusted to give maximum flocculation.

The optimum quantity of the colloidal polyamine-halohydrin resin that should be used to obtain the best retention of a dispersed or emulsified resin, wax, or other impregnating agent may vary with the nature and particle size of the dispersion, the nature of the cationic resin colloid, the time of contact between the pulp fibers and the polyamine resin solution, the pH of the stock and other factors. Also, because of the properties of the dispersed material added and the requirements of the finished sheet or article to be made, it may be desirable to modify the proportion of polyamine resin in order to obtain increased properties thereof in the finished product. In general, the proper amount of polyamine resin colloid required may vary from small amounts on the order of 0.1%, based on the weight of the paper stock, up to several times the weight of the impregnating agent. Larger quantities of the cationic polyamine-halohydrin resin are usually needed to obtain the maximum retention with decreasing quantities of impregnating agent, but good retention can be obtained at any desired ratio of impregnating agent to fiber by observing the proper operating conditions. When using relatively large quantities of impregnating agent, on the order of 50-100% or more of the weight of the cellulosic fibers, the optimum quantity of cationic resin is within the range of about 1-5%, based on the weight of resin solids in the impregnating agent. With smaller quantities of impregnating agent, such as 5-50% on the weight of the cellulose, larger quantities of the cationic resin on the order of 2-20% should be used. Larger quantities of the polyamine resin up to 100% or more on the weight of the impregnating agent may be added to modify the properties of the finished product if desired, but in such cases there is a definite falling off in the retention and also an increase in the drainage time of the stock. It is usually desirable to run trials with the specific dispersion of impregnating agent to be added, using the desired operating conditions, before deciding finally on the exact proportions of cationic polyamine-halohydrin resin to use.

Although a high degree of flocculation and retention of the added impregnating agent is obtained by the use of cationic polyalkylene-polyamine-halohydrin resins alone, it is sometimes

advantageous to add an additional precipitating agent during the stock preparation. Thus, for example, better drainage of water from the stock and reduced foam and press sticking are sometimes obtained when small quantities of alum on the order of 0.5-3%, based on the weight of the cellulosic material, are added. We can also add the normal amounts of sizes, fillers and other papermaking ingredients such as wax size, rosin size, calcium carbonate or clay fillers or pigments, starches, gums and the like to the stock, followed by precipitation with alum if necessary or desirable, either before or after treatment of the stock with the cationic alkylenepolyamine resin. In this case the alum or other precipitating agent, if it is used, is almost always added after the other ingredients have been mixed, in order to take advantage of the coagulating and precipitating action of the polyamine resin; however, in special cases where a preliminary coagulation may be desirable the alum or other electrolyte may be introduced ahead of the impregnating agent if desired.

The principles of the invention may be applied in a wide variety of fields of papermaking, moulding, laminating, extruding, preforming and the like and in general wherever a fibrous cellulosic material intimately associated with thermoplastic, thermosetting, waxy, bituminous or other type of bonding, impregnating or coating material is desired. The following are illustrative of some of the fields in which the invention may be employed.

PAPER AND BOARD MAKING

As is noted above, the principles of the present invention may be used to obtain a more uniform incorporation of large quantities of waxes, bituminous material and the like into paper stock before the sheet-making procedure. When the object is to obtain ink resistance, waterproofing and the like sizes such as rosin size or wax size are applied in relatively small amounts on the order of 1-5% or, in the case of asphalt, up to 10%, based on the dry weight of the paper stock. The cationic polyamine-halohydrin resin solution is first mixed with the aqueous stock suspension at any desired consistency, such as an 0.5-5% stock suspension in the beater chest and allowed to stand for 0.5-3 hours, after which the size is added in the form of an aqueous dispersion. Flocculation of the dispersed sizing material by the cationic polyamine resin takes place rapidly, and particles thereof, intimately mixed with the cationic resin are retained uniformly by the paper stock. The impregnated stock is then run out on the papermaking wire or cylinder and the resulting paper passed through heated drying rolls in the usual manner.

Light-weight papers having improved tearing strength, water resistance and other desirable properties may be obtained by incorporating dispersions of rubbers, polyacrylates, elastomers, and various copolymers by means of the process described. Properties of the sheets may be modified by heating, wet or dry pressing, calendering, hot calendering, friction calendering, plating and the like. Likewise the paper may be dried on a polished metal cylinder. By the use of this process cheaper and weaker pulps, such as ground wood, waste fibers, and short-fibered materials, may often be used while still obtaining good sheets properties.

Wall board, insulating board and heavy stock for paper containers may be made by the above

described procedure using the normal-sizing materials. Also, small amounts on the order of 5-10% of resins such as coumarone resin, polyindene resin, phenolic resins, residue from rosin purification, polystyrene resin and the like may be added either alone or in conjunction with these sizes to obtain improved water resistance, dimensional stability, rigidity, toughness and improved surface characteristics.

MANUFACTURE OF PAPER HAVING A HIGH RESIN CONTENT

Paper impregnated with large quantities of thermoplastic or thermosetting resins such as polystyrene, polyethylacrylate, modified or unmodified phenol-formaldehyde resins and the like may be used for a wide variety of purposes, such as for laminating by heat and pressure, in the manufacture of electrical insulators and condensers, in board moulding processes and the like. Quantities of resinous binders ranging from 5% up to considerably more than the weight of the fibrous cellulosic material can be incorporated by the following procedure:

A fibrous cellulosic material such as kraft paper pulp is hydrated by beating in the usual manner, preferably somewhat less than in the ordinary papermaking procedure. The stock is then diluted with water to a consistency of about 1-6% solids and a solution of cationic polyamine-halohydrin resin is added in amounts of about 0.5-15% of the amount of resinous binder to be incorporated into the stock. After thorough mixing the suspension is preferably allowed to stand for a short time, after which an emulsion or dispersion of the desired resin or resins is added with agitation. The stock is then formed into paper or paper board or may be moulded by any suitable pulp-moulding procedure.

In some cases it may be desirable to add an acid such as sulfuric acid or an alkali such as sodium or ammonium hydroxide to the stock solution after the cationic polyamine resin solution has been added but before introducing the resinous emulsion in order to control the final pH of the sheet. Likewise alum may be added to assist in controlling the pH, eliminating foam or stickiness, and modifying the draining characteristics of the stock.

Paper or paper board containing 5-75% on the basis of the finished sheet weight of resins, pitches, waxes and the like can be used for various purposes for which paper is ordinarily used but having improved strength resistance, weight resistance, water resistance, water vapor resistance, grease resistance, reduced expansion and contraction under varying humidity conditions, etc. In many instances full development of these desirable properties will depend upon mechanical treatments such as high temperature drying, cold or hot calendering and the like. Boards made in accordance with the present invention provide paper cartons and containers having improved protective properties, and costs can be held at a reasonable point by using dispersions or emulsions of cheap resinous materials. Wall boards, structural boards and papers, insulating boards, floor covering, shingles and the like may also be made by the same process.

Waxed or oiled papers can be made by incorporating high proportions of amorphous or crystalline waxes or mineral or vegetable oils in the form of emulsions or dispersions. Heating or hot calendering generally is required to develop maximum transparency and water resist-

ance. Strong and flexible papers having the properties of leather or cloth can be manufactured by incorporating synthetic or natural rubber latices, elastomers, and resins in suitable proportion. Heating, calendering, and other mechanical processing can be used to enhance the desired properties. Fire or flame resistance may be imparted to paper and paper board by incorporation of such materials as chlorinated waxes, polymers of chlorinated styrene, aminotriazine pyrophosphates such as melamine pyrophosphate and various thermosetting resins. Mineral fibers also may be incorporated at the same time to assist in obtaining maximum fire resistance.

PREFORMING AND MOULDING

Cellulose fibrous materials such a paper pulp impregnated with resinous binders by the process of this invention constitute an important article of commerce, for they can be dewatered and sold as such or lightly pressed into a cohesive mass. This mass may be preformed by suitable moulding procedures into shaped pieces for subsequent hot moulding processes or may be chopped, shredded, or ground (either in the dry or wet state) and used subsequently for impression, transfer, or injection moulding either alone or mixed with other types of moulding powders. When rubber latex or other forms of natural or synthetic rubber are coated on the fibers in the manner described above, the product can be worked on heated rolls wherein other fillers such as finely divided carbon black or zinc oxide may be incorporated together with curing accelerators such as mercaptobenzothiazole and antioxidants if desired after which the product can be cured by heating in moulds in the usual manner.

In the manufacture of large articles of irregular shape from moulding compositions containing a resinous binder together with a cellulosic filler considerable difficulty has been experienced in obtaining adequate draw or flow in all parts of the mould. To overcome this difficulty a technique preforming or premoulding has been developed, in which a uniform mixture of the resinous binder and filler is made into approximately the desired shape of the finished article without curing the resin. The process of the present invention is particularly well suited for preforming processes of this type, since the fibrous character of the filler is retained and therefore the preforming can be done by wet moulding processes. Moreover, there is much less loss of resin in the drainage water when operating in accordance with the principles of the present invention.

Preforms prepared with the aid of cationic polyamide-halohydrin resin solutions will simplify many moulding problems and increase the types of fillers and resins that may be moulded. Wood flour, cotton flocks, kraft paper stock and other standard materials may be used as well as macerated cellulosic fabrics such as canvas, cords and other fillers that impart increased toughness and impact strength to the moulded piece. Any of these fillers, or any desired mixture thereof can be suspended in water, treated with cationic polyalkylenepolyamine-halohydrin resin solution and then impregnated uniformly with thermosetting or thermoplastic resinous binders in the manner described above, after which they can be preformed into the desired shape by straining or forming on a screen or other permeable surface having the desired shape. Losses due to resins dissolved or suspended in the water

passing through the screen are usually less than 10%, and even these small quantities of resin can be readily recovered by reuse of the water. Phenol-formaldehyde and cresol-formaldehyde resins are advantageously applied by this method in amounts of 10-100%, based on the dry weight of the cellulosic fibers.

LAMINATING AND MOULDING

Sheets and boards impregnated with large quantities of thermoplastic or thermosetting resins by the process of the invention are particularly well suited for laminating and moulding processes by reason of the uniform distribution of the resinous material. Laminating paper is preferably made on an ordinary Fourdrinier machine or on a cylinder machine. Heavier board for moulding purposes is often made on a so-called "wet" machine, i. e. a paper-making cylinder feeding a drum on which the wet sheet may be wound until board of the desired thickness is obtained. When thermosetting resins are used a curing catalyst such as phthalic acid, oxalic acid and the like may be sprayed on the wet paper before it is dried or, in the case of phenol-formaldehyde resins, hexamethylene tetramine may be applied as a spray to the dried paper or board. Laminating is accomplished by pressing a stack of the impregnated sheets between hot platens. Moulding is accomplished either directly from the paper or board, used as a preform, or after the felted fibrous material is shredded or chopped to obtain better flow in the mould. Mouldings of high mechanical strength and impact resistance are obtained by this procedure.

The invention will be further illustrated by the following specific examples, which show preferred embodiments thereof. It should be understood, however, that the invention in its broader aspects is not limited to these examples, but that other modifications and variations in materials, quantities and procedures may be resorted to within the scope of the appended claims.

Example 1

Epichlorhydrin-alkylenepolyamine resin: A solution of 75.6 grams (0.4 mols) of tetraethylenepentamine in 112.6 grams of water was prepared and 37 grams (0.4 mols) of epichlorhydrin was added slowly with stirring while maintaining the temperature of the solution at about 50° C. Stirring was then continued at the same temperature for an additional 30 minutes after which the batch was stirred at 80° C. for a short time, whereby a 50% resin solution was obtained.

Emulsion No. 1: A solution of 1.2 parts by weight of "Duponol C" in 58.8 parts of water was heated to 94° C. and 0.05 parts of 40% hydrogen peroxide were added. To this solution 40 parts of styrene were introduced uniformly during 1.5 hours. The exothermic polymerization reaction proceeded smoothly and was complete after 3.5 hours. Steam was blown through the batch to remove unpolymerized material and the dispersion was adjusted to 25% solids. "Duponol C" is a higher alkyl sulfate (molecular weight 350) containing 10.8% Na₂SO₄ and 3.4% moisture.

Emulsion No. 2 was a polystyrene emulsion prepared exactly as described for Emulsion No. 1, but 2 parts by weight of sodium petroleum sulfonate was used instead of the "Duponol C."

Emulsion No. 3: To a solution of 5 parts by weight of "Duponol C" in 145 parts there was added 0.5 parts of 30% hydrogen peroxide and the solution was heated to 94° C. A mixture of

50 parts by weight of styrene and 50 parts of ethyl acrylate was introduced uniformly during 1.5 hours, after which the procedure of Emulsion No. 1 was followed.

These resins were used in the preparation of hardboard. Pine chips were cooked 30 minutes with steam at 100 lbs./sq. in. pressure, and defibered. The pulp was diluted with water to 2% solids, a solution of the epichlorhydrin-polyamine resin was added and mixed thoroughly and the mixture was allowed to stand at least one-half hour. The polystyrene or styrene-ethyl acrylate copolymer emulsion was then added slowly and stirring was continued until the filtrate from a sample was clear, showing a good retention of resin on the fibers.

The stock was made into board on a handsheet machine by diluting to 1% fiber consistency and felting with a vacuum of 11 inches of mercury. The sheets, having an area of 72 square inches, were pressed between a wire screen and a polished steel platen to remove excess water and the wet board was hot pressed between 1/8-inch stops, to give a standard thickness, at 350° F. for 15 minutes using about 1,500 lbs./sq. in. pressure. The dense boards were cooled under slight pressure and tested for modulus of rupture with a conventional beam tester.

In the following table the amounts of resins are expressed as per cent of the weight of the dry fiber used, and these amounts express the actual weight of resin solids and do not include the weight of solvent or aqueous phase of the emulsions. The fiber weights are dry weights expressed in grams while the modulus of rupture is given in pounds per square inch.

Sample No.	Fiber Weight	Cationic Resin	Emulsion No.	Amount	Drainage Time, Sec.	Mod. of Rupture
1	149				49	2,318
2	133	0.75	1	5	71	5,365
3	126	1.0	1	10	74	9,965
4	93	1.5	1	50	150	11,210
5	70	2.0	1	100	360	11,380
6	126	1.0	2	10	83	10,000
7	93	1.5	2	50	209	12,225
8	126	1.0	3	10	88	11,025
9	140	10.0				9,260

These results show that polystyrene and styrene-ethyl acrylate copolymer resins can be applied to cellulosic fibers in any desired propor-

hydrin-polyamine resins. Substantially complete retention of the emulsified thermoplastic resin is obtainable with as little as 0.75% of the polyamine resin, based on the weight of the fibers, when relatively small amounts of polystyrene are applied. Larger amounts on the order of 1.5-2% of the polyamine resin will effect a substantially complete retention of 50-100% of polystyrene.

Example 2

15-gram batches of bleached kraft pulp, beaten to a Greene freeness of 475-500, were suspended in water to about 1.5% consistency and treated with varying amounts of the epichlorhydrin-tetraethylenepentamine resin described in Example 1. After 3 hours aging the pH was adjusted to 6.5-7.0 and an emulsion of wax or polystyrene resin was added in an amount equal to the dry weight of the fiber. The mixtures were then stirred for 5 minutes, or longer if the filtrate from a sample remained turbid, and were then diluted with water to 1% fiber and 200-gram portions were used to form handsheets on a laboratory handsheet machine. The retention of wax or resin was calculated from the gain in weight of the sheet over the fiber weight. The following wax emulsions were used.

Wax Emulsion No. 1: A mixture of 225 parts by weight of molten scale wax and 22 parts of oleic acid was added to 250 parts of hot water containing 2.6 parts of NaOH followed by heating for 15 minutes and homogenizing to a smooth emulsion of 1-2 microns particle size.

Wax Emulsion No. 2: 250 parts by weight of molten scale wax were added to 250 parts of hot water containing 5 parts of "DuPont C" followed by homogenizing to a smooth emulsion.

Polystyrene Emulsion: This was No. 1 of Example 1.

In the following tables, which show the results obtained, the top row gives the amount of epichlorhydrin-polyamine added as per cent of the dry weight of the fibers and the bottom row shows the resin retention as per cent of the total resin added; i. e. wax or polystyrene plus epichlorhydrin-polyamine resin. The presence of cloudiness in the white water after the first mat of fibers is formed on the screen indicates an incomplete flocculation of the emulsified wax or polystyrene by the cationic resin, whereas a clear white water indicates an almost complete flocculation.

WAX EMULSION NO. 1

Per cent Cationic Resin	0	1	2	3	5	10
Drainage Time, sec.	26	33	42	43	40	35
White Water	Clear	Cloudy	Cloudy	Sl. cloudy	Clear	Clear
Sheet Weight, grams	2.03	2.29	2.96	3.53	3.67	3.61
Retention		12.9	45.6	72.8	78.2	71.8

WAX EMULSION NO. 2

Per cent Cationic Resin	0	1	2	3	5	10
Drainage Time, sec.	19	42	41	36	35	34
White Water	Clear	Sl. cloudy	Clear	Clear	Clear	Clear
Sheet Weight, grams	2.02	3.00	3.55	3.65	3.67	3.59
Retention		48.5	75.0	79.2	78.7	71.4

POLYSTYRENE EMULSION

Per cent Cationic Resin	0	1	2	3	5	10
Drainage Time, sec.	18	22	55	80	71	52
White Water	Clear	Cloudy	Clear	Clear	Clear	Clear
Sheet Weight, grams	1.97	2.85	3.79	3.80	3.90	3.92
Retention		43.1	89.3	88.9	91.8	88.7

tions up to 100% of the weight of the fiber without difficulty by the application of cationic halo-

These results show that good retentions of waxes and resins are obtained when relatively

small amounts of halohydrin-alkylenepolyamine resins on the order of 1-10% are used, even with quantities of impregnating materials equal to the weight of the cellulose fibers.

Example 3

The procedure of Example 2 was followed, but a thermosetting polyamine-halohydrin prepared by the following procedure was used:

A solution of 37.8 parts by weight (0.2 mols) of tetraethylenepentamine in 93 parts of water was prepared and epichlorhydrin was added slowly with stirring at a rate such that the reaction temperature did not rise above 50° C. After 35.5 parts (0.6 mols) of epichlorhydrin had been added the stirring was continued at 50° C. until the product became viscous. The resulting hydrophilic colloid was diluted with water to a 15% solution.

The wax emulsions and polystyrene emulsion were the same as in Example 2. The results are shown in the following tables, where the figures have the same meaning as the corresponding figures in that example.

WAX EMULSION No. 1

Per cent Cationic Resin.....	0	2	3	4	5	10
Drainage Time, sec.....	25	37	40	40	33	33
White Water.....	Clear	Cloudy	Cloudy	Sl. cloudy	Clear	Clear
Sheet Weight, grams.....	2.07	3.25	3.27	3.38	3.63	3.83
Retention.....		57.9	58.3	63.1	74.3	80.0

WAX EMULSION No. 2

Per cent Cationic Resin.....	0	1	2	3	5	10
Drainage Time, sec.....	21	16	25	26	23	44
White Water.....	Clear	Cloudy	Clear	Clear	Clear	Cloudy
Sheet Weight, grams.....	2.09	3.56	3.65	3.58	3.61	3.31
Retention.....		72.8	76.6	72.4	72.4	55.5

POLYSTYRENE EMULSION

Per cent Cationic Resin.....	0	1	2	3	5	10
Drainage Time, sec.....	20	10	15	34	60	83
White Water.....	Clear	Cloudy	Sl. cloudy	Clear	Clear	Cloudy
Sheet Weight, grams.....	1.97	2.42	3.40	3.87	3.86	3.11
Retention.....		22.3	70.2	92.3	90.2	51.8

Example 4

The principles of the present invention may be applied to the impregnation of cellulosic fibers such as groundwood, steam-treated or exploded wood fibers, kraft paper stock or other types of paper pulp with emulsions of thermosetting resins such as phenol-aldehyde resins, alkyd resins and the like. One important class of alkyd resins that may be used for impregnation or coating by this method is the thermosetting polybasic acid-polyhydric alcohol alkyd resins copolymerized with a polymerizable unsaturated organic compound having a boiling point above 60° C. which contains at least one H₂C=C group and is free from double bond systems in conjugation therewith such as styrene and methyl styrenes, diallyl phthalate, methyl methacrylate, diallyl maleate or fumarate and the like. Typical resin emulsions of this class are the following:

Alkyd Resin Emulsion A: An alkyd resin is prepared by heating a mixture of 3.6 mols of ethylene glycol and 3 mols of diethylene glycol with 4 mols of fumaric acid and 2 mols of phthalic anhydride for about 8 hours at 180° C. This resin is dissolved in about 25% of its weight of diallyl phthalate. 35 parts by weight of this product are agitated while adding a

solution of 40 parts of 10% potassium stearate and 0.5 parts of sodium isopropyl naphthalene sulfonate in 24.5 parts of water followed by homogenizing to a particle size of 1-2 microns.

- 5 Alkyd Resin Emulsion B: A solution containing 1.6 parts by weight of gum arabic, 0.5 parts of lignin sulfonate, 0.6 parts of boric acid and 49.8 parts of water is prepared and mixed with 47.5 parts of the same alkyd resin solution.
- 10 This mixture is homogenized to 1-2 microns particle size.

Typical phenol-formaldehyde resin emulsions are:

- 15 Phenol Resin Emulsion: A mixture was prepared containing 200 parts by weight of phenol, 146 parts of 37% aqueous formalin, 0.3 parts of sodium alkyd sulfate wetting agent (molecular weight about 300-330), 2.8 parts of methyl cellulose, 2 parts of 18.4% hydrochloric acid and 200 parts of water and heated with agitation for about 40-50 minutes at 90-100° C., or until a phenol-formaldehyde resin emulsion was obtained.

Bleached kraft paper pulp was beaten to a

- Greene freeness of 475-500 and then used to make a number of stock suspensions, each containing sufficient fiber to make a sheet weighing approximately 2 grams suspended in water at 1.5% consistency. Cationic tetraethylenepentamine-epichlorhydrin resin solution was added to some of these suspensions in the amounts indicated below, the remainder being used as controls, and the suspensions were allowed to age 3 hours before treatment. The pH of the resin-containing samples was then adjusted to 6.5-7 and one of the above-described resin emulsions was added in the amount indicated in the following tables. The stock was then made into handsheets on a small sheet-making machine provided with a graduated glass stock cylinder so that the rate of drainage could be measured accurately. The sheets were dried at 160° F. and weighed and the total resin retention and resin content was determined from the increase in weight. In the following tables the per cent of cationic resin is based on the actual weight of resin solids in the emulsion added and the per cent of emulsion represents resin solids based on the dry weight of the fiber. The degree of clarity of the white water is determined after a mat of fibers has been formed on the sheet-making wire, and indicates the completeness of flocculation of the dispersed resin.

ALKYD RESIN EMULSION A

Cationic Resin of	Per Cent Cationic Resin	Per Cent Emulsion	Drainage Time, sec.	White Water	Dry Sheet Wt. Grs.	Per Cent Retention	Per Cent Resin in Sheet
Example 1	None	None	22		2.00		
	3	100	24	Clear	3.65	76.8	45.2
	5	100	19	do	3.83	83.6	47.8
	5	125	16	do	4.01	72.0	49.4
	5	150	15	do	4.44	73.1	54.3
Example 3	10	100	17	do	3.83	80.0	47.8
	5	125	11	do	4.28	81.8	52.6
	10	150	10	do	4.63	78.8	56.3

ALKYD RESIN EMULSION B

Cationic Resin of	Per Cent Cationic Resin	Per Cent Emulsion	Drainage Time, sec.	White Water	Dry Sheet Wt. Grs.	Per Cent Retention	Per Cent Resin in Sheet
Example 1	None	None	17		2.07		
	2	100	26	V. Sl. Cloudy	3.22	5.64	35.8
	5	100	24	do	3.03	45.7	31.7
Example 3	10	100	23	Clear	3.40	60.5	39.2
	2	100	25	do	3.49	69.7	40.7
	5	100	28	Cloudy	3.13	50.5	33.8
	10	100	30	Very Cloudy	2.74	30.4	24.4

PHENOL RESIN EMULSION

Cationic Resin of	Per Cent Cationic Resin	Per Cent Emulsion	Drainage Time, sec.	White Water	Dry Sheet Wt. Grs.	Per Cent Retention	Per Cent Resin in Sheet
Example 1	None		18		2.11		
	3	100	21	Clear	3.38	61.7	37.6
	5	100	21	do	3.37	60.0	37.4
	10	100	25	do	3.42	59.6	38.3
	3	100	29	Slightly Cloudy	3.24	54.8	34.9
	5	100	41	do	3.21	52.4	34.3
	10	100	42	do	2.83	32.7	25.4

Example 5

Coumarone Resin No. 1: An 80% solution of "Cumar RH" in xylene was prepared and 50 parts by weight were added to an aqueous solution prepared by dissolving 2 parts by weight of 25% sodium dioctyl sulfosuccinate and 1.5 parts of "Tween 40" (a condensation product of ethylene oxide with sorbitan monopalmitate) in 46.5 parts of water. The mixture was homogenized to an emulsion of fine particle size to which 20 parts of water were added. The xylene was then stripped out in a distillation column, leaving a dispersion containing 45% of coumarone in a water solution containing 2% of emulsifying agents.

Coumarone Resin No. 2: The same emulsifying procedure was followed but "Cumar DX," a

The final emulsion contained 40% of coumarone resin and 2% emulsifying agents.

Batches of bleached kraft pulp was suspended in water and pretreated with 1% of the epichlorhydrin-tetraethylenepentamine resin of Example 1 followed by adding one of the above coumarone resin emulsions and forming the stock into sheets, using the procedure described in Example 2. The sheets were dried to constant weight by heating at 150° F. The amounts of resin added, based on the dry weight of the pulp, and the results obtained are given in the following table, wherein the water absorption is the amount taken up after soaking 2 minutes in cold water, expressed as per cent of the dry weight of the paper, and the tensile strength is given in pounds per inch width.

Sheet No.	Percent in Sheet	Basis Weight	Tensile Strength		Water Absorption	Stiffness-Gurley	
			Dry	Wet		Dry	Wet

RESIN NO. 1

1-A	None	120.5	57.7	2.0	139	1320.9	227.5
1-B	14.3	123.0	59.2	19.7	69.5	1382.5	365.8
1-C	23.8	123.0	58.5	19.7	59.5	1265.4	349.7
1-D	26.1	125.0	62.5	18.8	62.7	1431.9	443.9
1-E	40.9	128.0	43.4	28.4	40.6	1143.3	355.2
1-F	52.0	146.0	61.6	28.0	43.0	1882.0	555.0

RESIN NO. 2

2-B	16.6	117.5	51.5	16.3	127.1	1254.3	299.7
2-C	25.0	124.5	40.9	15.4	106.2	1221.0	305.3
2-D	33.3	124.0	42.0	12.0	103.3	1021.4	222.0
2-E	41.2	121.0	38.2	12.6	93.8	843.6	183.2
2-F	49.2	127.5	38.1	12.1	76.9	843.6	244.3

somewhat darker coumarone resin, was used.

The sheets were then pressed for 5 minutes at

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500 lbs./sq. in. between platens heated at 150° F. after which the water absorption, tensile strength and stiffness were again determined. The results were:

Sheet No.	Tensile Strength		Per Cent Water Absorption	Stiffness-Gurley	
	Dry	Wet		Dry	Wet
RESIN NO. 1					
1-A-----	55.6	2.1	125.3	999.0	199.8
1-B-----	65.2	22.8	66.6	1243.2	366.4
1-C-----	64.6	23.4	61.1	954.1	299.7
1-D-----	66.8	27.6	52.4	666.0	310.8
1-E-----	58.6	42.7	35.4	832.5	310.8
1-F-----	63.3	41.4	36.0	1287.6	527.3
RESIN NO. 2					
2-B-----	56.0	19.2	86.6	1043.4	321.9
2-C-----	70.2	24.4	62.7	1122.2	383.0
2-D-----	50.1	16.4	66.6	854.7	267.0
2-E-----	51.5	19.0	51.3	510.6	194.3
2-F-----	48.9	21.2	43.1	721.5	299.7

These results show that coumarone resin can be applied by the process of the invention for the manufacture of board, such as corrugated box-board, and that greatly increased wet strength and substantial improvements in other properties can be obtained therewith.

Example 6

A solution of 94.5 grams (0.5 mols) of tetraethylenepentamine in 492 grams of water was prepared and 161.2 grams (1.25 mols) of dichlorohydrin (ClCH₂.CH(OH).CH₂Cl) was added slowly with agitation while maintaining the temperature below 20° C. The syrup was then cooled to 10° C. and a solution of 51.5 grams of 97% NaOH in 150 grams of water was added. The mixture was agitated for 3 hours to initiate the formation of a thermosetting resin. The resulting resin syrup had a pH of 8.0 and a solids content of 22%.

A water suspension of 15 grams of bleached Kraft paper pulp, diluted to a fiber consistency of 1.56%, was treated with a quantity of the above resin syrup such that 5% resin solids were added, based on the dry weight of the fiber. After adding the resin the suspension was allowed to stand for several hours at a pH of 5.1. The pH was then adjusted to 6.5 with dilute sodium hydroxide solution and a quantity of the polystyrene emulsion No. 1 of Example 1 was added equivalent to 15 grams of resin solids, or 100% resin on the weight of the fiber. The mixture was diluted with water to 1500 grams, so that the suspension contained 1% by weight of fiber and was stirred 15 minutes. 200-gram portions were then made into paper on a laboratory handsheet machine along with an equal number of control sheets containing no resin.

The average dry weight of the sheets prepared from the resin-treated stock was 3.83 grams, whereas the average of the blank sheets was 2.09 grams, thus indicating an 83% retention of the resins.

What we claim is:

1. A method of impregnating fibrous cellulosic material with a hydrophobic organic impregnating agent while preserving the freeness and felting properties thereof which consists in preparing a water suspension of the fibrous cellulosic material at 0.5-6% consistency, adding to said suspension a hydrophilic cationic alkylenepolyamine-epichlorhydrin resin in amounts of 1-20%

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of the weight of the organic impregnating agent, aging the suspension at a pH of about 3 to about 8 for at least 30 minutes, then adding an aqueous dispersion of the impregnating agent in deflocculated condition, flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic alkylenepolyamine-epichlorhydrin resin, and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibres.

2. A method of impregnating fibrous cellulosic material with approximately 50-100% of its weight of a hydrophobic organic impregnating agent which consists in preparing a water suspension of the fibrous cellulosic material at 0.5-6% consistency, adding to said suspension a hydrophilic cationic polyamine-epihalohydrin resin in amounts of at least 1% of the weight of the organic impregnating agent, aging the suspension at a pH of about 3 to about 8 for at least 30 minutes, then adding the requisite quantities of an aqueous dispersion of the impregnating agent in deflocculated condition, flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic polyamine-epihalohydrin resin, and thereby depositing approximately 50-100% by weight of the impregnating agent uniformly on said fibres, said weight of deposited impregnating agent being based on the weight of said fibers.

3. A method of impregnating fibrous cellulosic material with approximately 50-100% of its weight of a hydrophobic organic impregnating agent which consists in preparing a water suspension of the fibrous cellulosic material at 0.5-6% consistency, adding to said suspension a hydrophilic cationic alkylenepolyamine-epihalohydrin resin in amounts of at least 1% of the weight of the organic impregnating agent, aging the suspension at a pH of about 3 to about 8 for at least 30 minutes, then adding the requisite quantities of an aqueous dispersion of the impregnating agent in deflocculated condition, flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic alkylenepolyamine - epihalohydrin resin, and thereby depositing large quantities on the order of 50-100% by weight of the impregnating agent uniformly on said fibres, said weight of deposited impregnating agent being based on the weight of said fibers.

4. A method for the production of felted fibrous cellulosic material having a uniform content of a hydrophobic organic impregnating agent which consists in preparing a water suspension of the fibrous cellulosic material, adding to said suspension a solution of hydrophilic cationic polyamine-epihalohydrin resin, aging the resulting suspension at a pH of about 3-8 for at least 30 minutes, adjusting the pH of the suspension to about 6.5-7.0, and then adding an aqueous dispersion of the impregnating agent in a deflocculated condition, flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic polyamine-epihalohydrin resin and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibres and forming the impregnated fibres into a felted product while draining the suspending water therefrom.

5. A method of incorporating a water-insoluble hydrophobic impregnating agent uniformly into fibrous cellulosic material which consists in adding a hydrophilic cationic polyamine-epihalohydrin resin to a water suspension of said fibrous

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cellulosic material, adding to said suspension an aqueous dispersion of the impregnating agent in deflocculated condition and a compound selected from the group consisting of anionic and non-ionic emulsifying agents, flocculating the impregnating agent by the action of the cationic polyamine-epihalohydrin resin in the cellulosic fibrous suspension, and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibres.

6. In a method of making a formed cellulosic product by the steps of preparing an aqueous suspension of fibrous cellulosic material, impregnating the cellulosic material with a water-insoluble hydrophobic organic impregnating agent and forming the impregnated cellulosic material into a felted product, the improvement which consists in first adding a solution of a hydrophilic cationic polyamine-epihalohydrin resin to the aqueous fiber suspension, then adding an aqueous dispersion of the impregnating agent in deflocculated condition and flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic polyamine-epihalohydrin resin and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibres.

7. A method according to claim 6 in which the polyamine-epihalohydrin is an alkylene polyamine-epichlorhydrin resin.

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