

Aug. 14, 1951

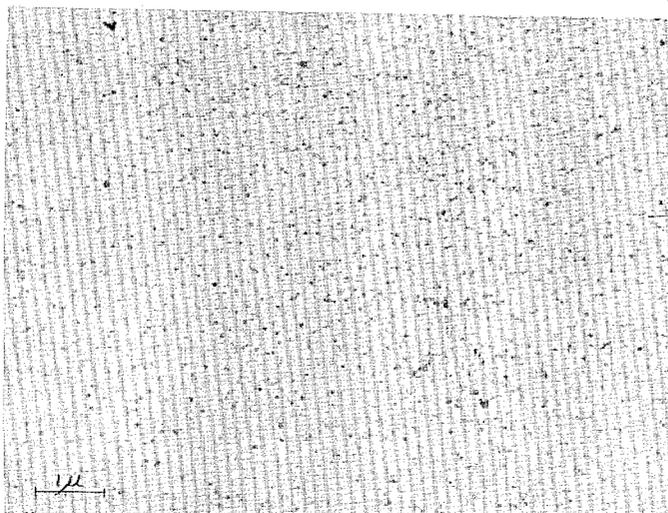
L. H. WILSON ET AL
SIZING CELLULOSIC FIBERS WITH CATIONIC MELAMINE
RESIN AND HYDROPHOBIC MATERIAL

2,563,897

Filed July 13, 1945

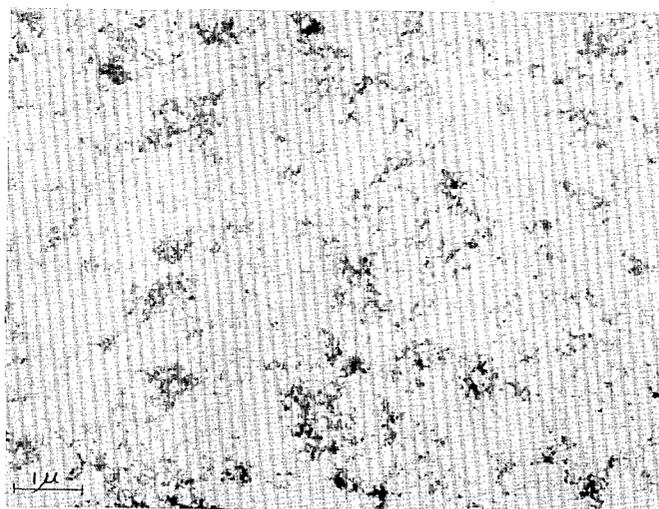
5 Sheets-Sheet 1

Fig. 1.
7



14,000 X

Fig. 2.
7



14,000 X

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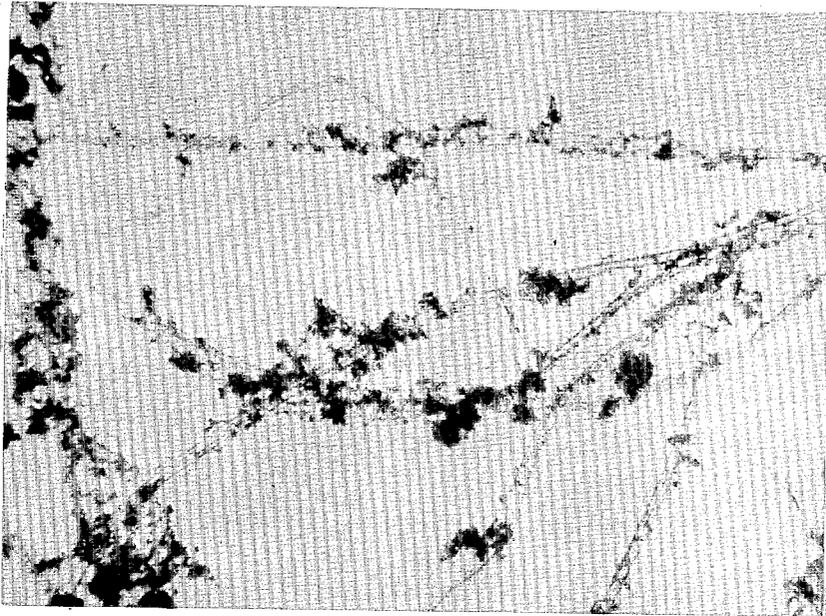
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5 Sheets-Sheet 2

Fig. 3



75 X

Fig. 4



75 X

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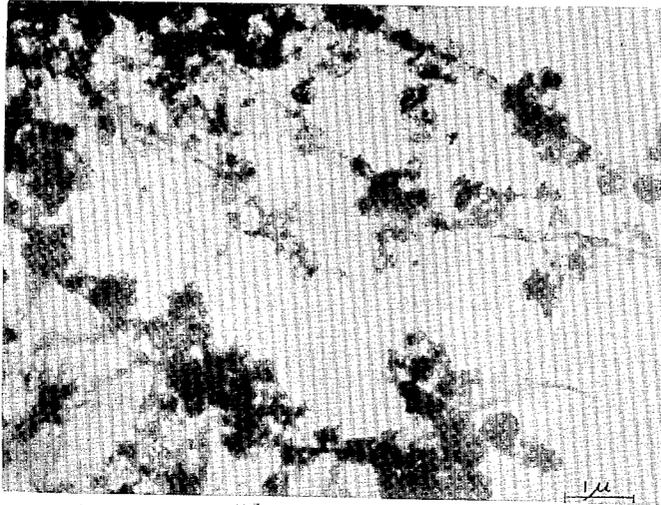
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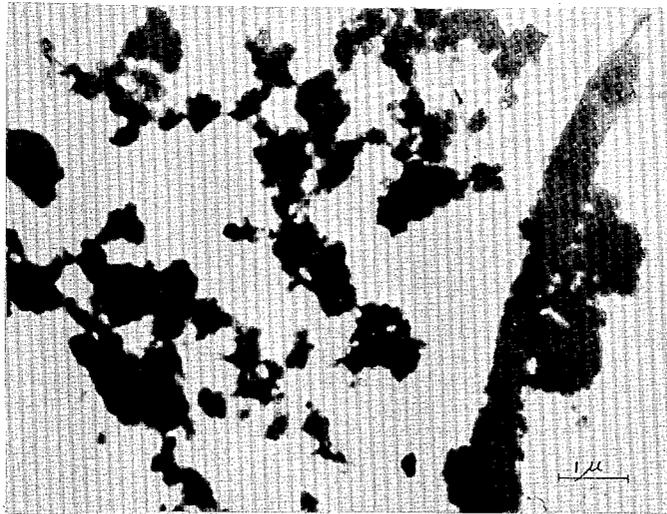
5 Sheets-Sheet 3

Fig. 5.



14000 X

Fig. 6.



14000 X

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5 Sheets—Sheet 4

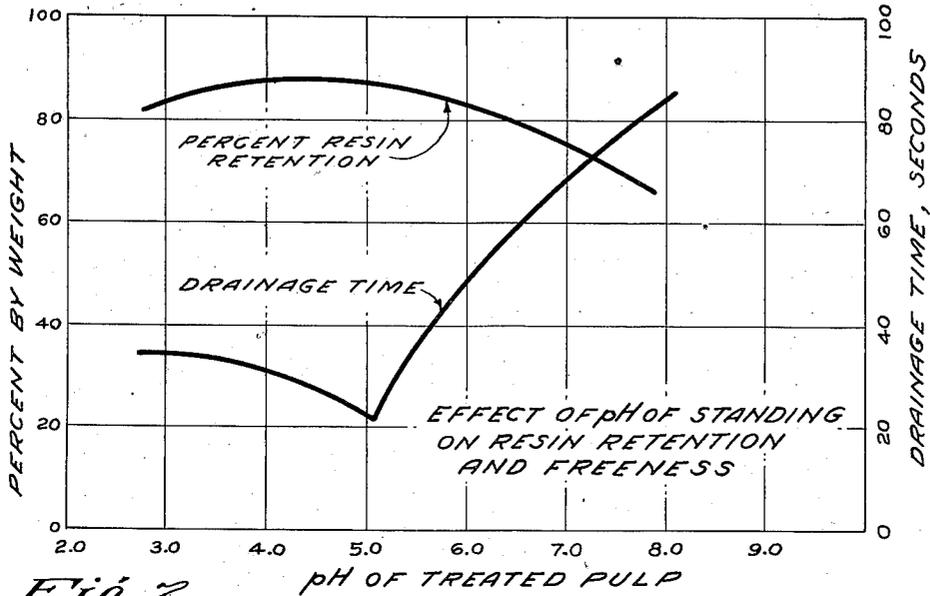


Fig. 7.

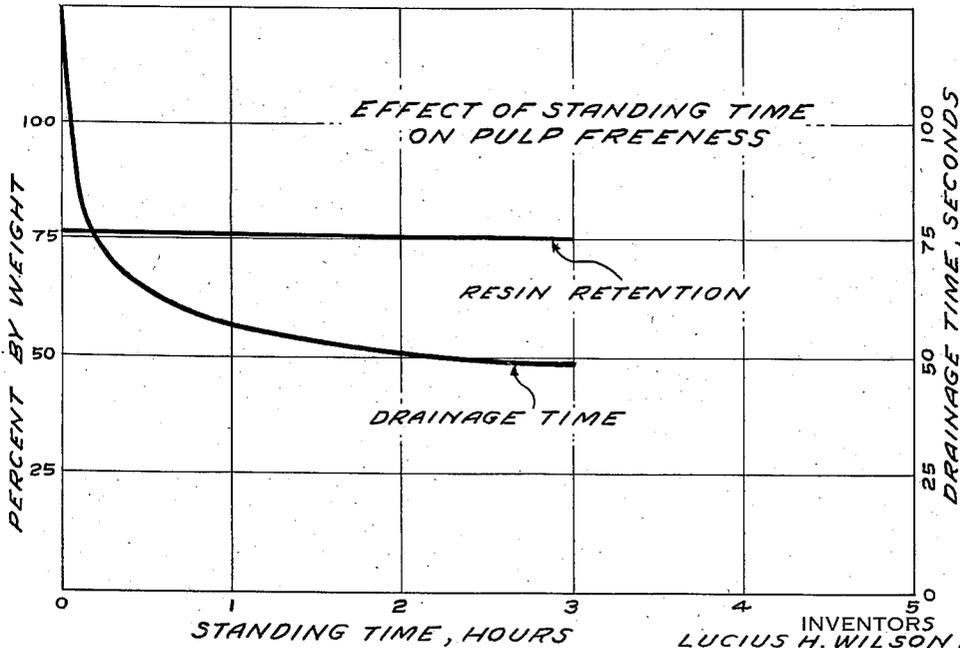


Fig. 8.

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5 Sheets-Sheet 5

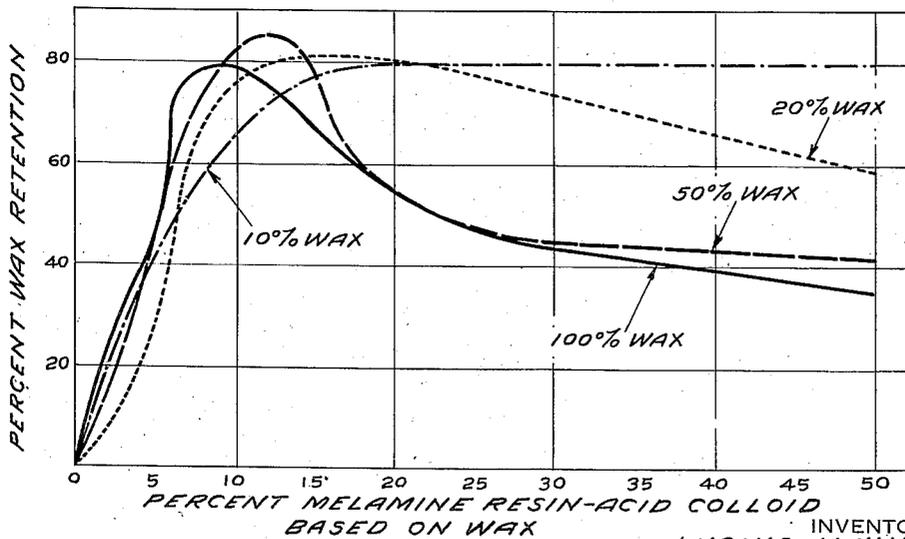
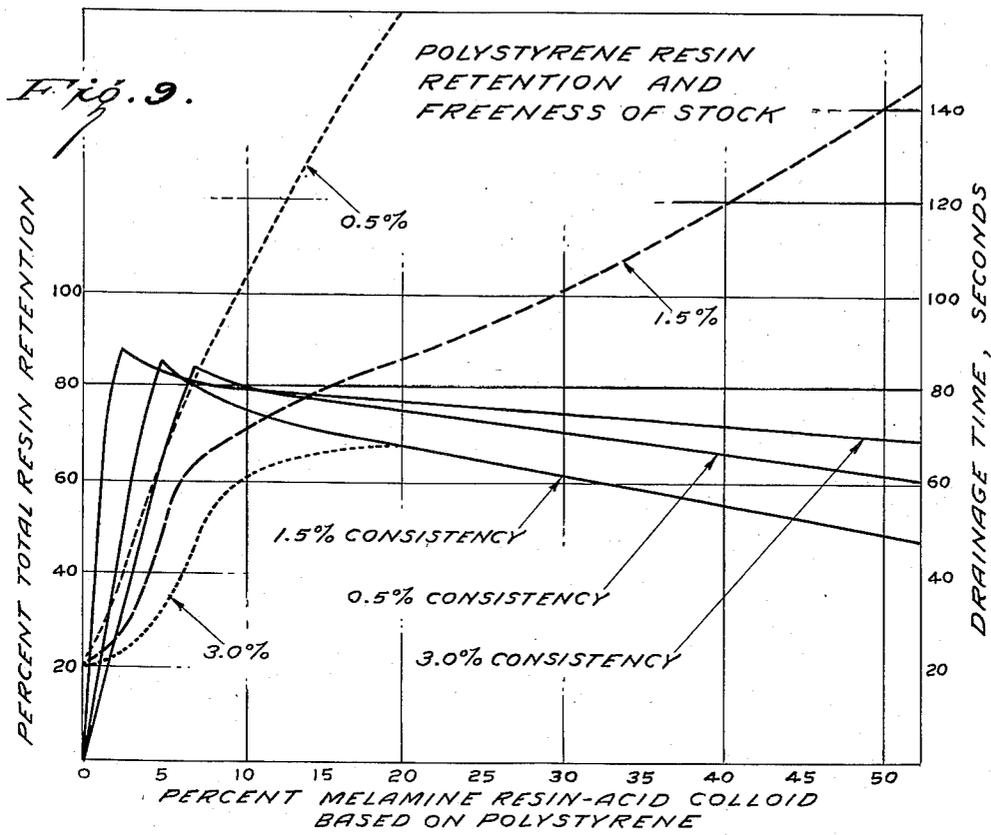


Fig. 10.

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UNITED STATES PATENT OFFICE

2,563,897

SIZING CELLULOSIC FIBERS WITH CATIONIC MELAMINE RESIN AND HYDROPHOBIC MATERIAL

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Application July 13, 1945, Serial No. 604,904

10 Claims. (Cl. 92-21)

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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% to 5% on the weight of the fiber. However, serious operating difficulties are frequently encountered when attempts are made to

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incorporate larger quantities of impregnating agents 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 sizes. 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

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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, alkyl resins and the like may be incorporated into paper stock in the quantities necessary for pre-moulding 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 our 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.

Our invention is based on the discovery of an unusual type of flocculation and deposition that is brought about by the action of cationic melamine-aldehyde 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. We have found that in such a system the cationic melamine-aldehyde 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, we have found that the cellulose 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 cellulose fibers themselves. Moreover, when the proper quantities of cationic melamine-aldehyde 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 and deposition of organic material in the white water system is avoided.

Figures 1 to 6 are views of photomicrographs. Figures 7 to 10 are graphs illustrating various comparative tests.

Fig. 1 is an electronmicrograph of emulsion-polymerized polystyrene and Fig. 2 is a similar micrograph of the same dispersion after it has been flocculated by adding a cationic melamine-aldehyde resin colloid.

Fig. 3 is a photomicrograph showing cellulose fibers pretreated with cationic melamine-aldehyde resin and having polystyrene resin particles distributed thereon, while Fig. 4 is a similar

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photomicrograph in which the resin was coagulated with alum.

Figs. 5 and 6 are electronmicrographs of cellulose fibers coated with polystyrene in quantities of 50% and 100%, respectively, based on the dry fiber weight.

Figs. 7 and 8 are graphs showing, respectively, the effect of pH of standing and of time of standing on the pulp freeness.

Figs. 9 and 10 are similar graphs showing the effect of varying quantities of colloidal melamine resin on the retention of polystyrene and wax in dispersed condition.

The process of our invention 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 melamine-aldehyde resin. The distinctive type of flocculation that is obtained when an aqueous solution of cationic melamine-aldehyde resin colloid is added to an aqueous dispersion such, for example, as an emulsion-polymerized polystyrene dispersion is shown in Figs. 1 and 2 of the drawings, and 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 we have also found, as one of the most important features of our invention, that the distinctive flocculating action of the cationic melamine-aldehyde resin colloid continues, and is in many cases actually enhanced, after the cationic melamine resin has been adsorbed on the fibrous cellulosic material. The importance of this discovery resides in the fact that the melamine resin, being distributed uniformly over and through the cellulose fibers, causes a uniform deposition and retention of the impregnating agent on the fibers after it has been flocculated. This discovery has enabled us to deposit large quantities of any desired impregnating agent 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.

The distinctive manner in which the impregnating agent is deposited uniformly along the entire length of cellulose fibers containing an adsorbed layer of cationic melamine-aldehyde resin is most clearly shown by reference to Fig. 3 of the drawings, which is a photomicrograph at the relatively low magnification of 75 diameters. Fig. 4, which is included for purposes of comparison, is a similar photomicrograph in which the resin was coagulated by the addition of alum, no melamine-aldehyde colloid being used. It will be seen from Fig. 3 that the cationic melamine-aldehyde resin causes the flocculated polystyrene resin particles to be distributed in relatively finely divided condition along the cellulose fibers, whereas in Fig. 4 the fibers themselves are almost completely devoid of resin.

In an aqueous dispersion of fibrous cellulosic material to which a cationic melamine-aldehyde resin and an aqueous dispersion of an impregnating agent have been added, it will therefore be seen that two types of flocculation are occurring. That portion of the cationic melamine-aldehyde resin which has adsorbed on the cellu-

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losic fibers exerts both a flocculating and a clustering action, as described above. Free or unadsorbed melamine-aldehyde resin colloid, if present in the system, causes the distinctive type of flocculation shown in Fig. 2 of the drawings, and the flocs so produced are largely deposited on or entangled with the impregnated cellulosic fibers, either immediately or during subsequent felting or forming steps. The net result of this combined action is to retain large quantities of the impregnating agent on the cellulosic material in a uniform and well-distributed condition after the water has been drained from the system.

Although our invention is not dependent on any particular theory of operation, we offer the following 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 melamine resin colloid are adsorbed upon and retained by the cellulosic fibers when the cationic melamine resin solution is added to an aqueous suspension thereof. We believe, 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 melamine-aldehyde resin, over and above that required to impart a positive charge on the cellulosic fibers, the unadsorbed positively charged melamine-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 melamine-resin colloid and particles of the added emulsion or dispersion. These flocs or aggregates of combined resins, by reason 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 melamine-aldehyde resin colloid and other factors, to obtain complete or nearly complete retention of both the melamine

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resin and almost any desired proportion of organic impregnating agents.

Although the foregoing represents what we regard as the most probable explanation of the phenomena involved, the process of our 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 melamine resin colloid particles attached thereto, as well as the excess melamine resin colloid 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 melamine resin coated fibers, as well as the melamine resin colloid 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 melamine resin colloid solution.

The flocculating agents which we employ in practicing our invention, and which are designated for convenience as "cationic melamine-aldehyde resins," are resinous materials containing melamine and carrying a positive electrical charge when in aqueous solution. These colloidal resin solutions may be prepared by dissolving ordinary melamine-aldehyde condensation products, such as methylol melamines in acids such as hydrochloric acid to form acidified or "acid-type" resin solutions having a glass electrode pH value within the range of about 0.5 to about 3.5 when measured at 15% solids, or pH values up to 4.5 when measured in more dilute solutions, followed by aging to the colloidal condition, as described in U. S. Patent No. 2,345,543.

Another class of cationic melamine-aldehyde resins that may be used in practicing the present invention are the resinous copolymers of melamine, urea and aldehydes such as formaldehyde containing at least 0.7 mols of melamine for each 4 mols of urea and about 1-4 mols of combined formaldehyde for each mol of melamine+urea that are described in U. S. Patent No. 2,485,079. These cationic melamine resin copolymers are obtained by first preparing an acidified aqueous solution of an aldehyde condensation product of melamine and urea containing 1-70 mol per cent of urea and 30-99 mol per cent of melamine and about 0.2-1.5 mols of acid per mol of melamine, depending on the strength of the acid, and aging the solution until the colloidal cationic condition is reached. The essential requirement of aminotriazine-aldehyde condensation products used as flocculating agents in the process of our invention is that they be in the water-dispersible or hydrophilic partially polymerized condition and that they carry a positive electrical charge, and any suitable aminotriazine-aldehyde resin possessing these characteristics may be employed.

Any water-insoluble coating or impregnating agent may be applied by the process of our 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 our 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
crude scale wax
carnauba wax
montan wax
petrolatum
microcrystalline or amorphous petroleum wax
chlorinated waxes

Bituminous:

asphalt
tars and pitches
bitumens

Gums, etc.:

gum tragacanth
gum ghatti
gum elemi
starches
methyl cellulose

Rosins:

wood rosin
gum rosin
heat-treated or disproportionated rosin
acid-treated or polymerized rosin
hydrogenated rosin
limed rosin
sulfur-treated rosin

Elastomers:

natural latices
synthetic latices
isoprene polymers
neoprene polymers
butadiene polymers
copolymers of butadiene, isoprene, etc., with acrylonitrile

Resins—Thermosetting:

thermosetting phenol-aldehyde resins including particularly the phenol and alkyl-phenol formaldehyde moulding resins
urea-aldehyde 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 glycerin, pentaerythritol, dipentaerythritol, polyallyl alcohols, etc.

resins from melamine and higher aldehydes

polyindene resins

coumarone resins

vinylacetylene resins

"Vinsol" resin; i. e. residue from purifying wood rosin

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 melamine-formaldehyde 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 we have employed with success are the soaps of aliphatic and cycle-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 sulfocarboxylic acids such as esters of sodium sulfoacetate, dialkyl sulfosuccinamates, disodium monoalkyl sulfosuccinamates; amides of sulfocarboxylic 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 $\text{HO}(\text{CH}_2\text{O})_n\text{CH}_2\text{OCH}(\text{COOR})\text{CH}_2\text{COOR}$; 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 ad-

sorbing cationic melamine-aldehyde 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 stock, rag stock, soda, sulfate, ground-wood, sulfite stock and alpha pulp. Similarly, other forms of fibrous cellulose such as hydrated 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 non-cellulosic, 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, premoulded 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 to hydrate the cellulose, 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 melamine-aldehyde 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 melamine resin by the paper stock is quite rapid, but the subsequent behavior of the impregnated stock on a paper-making machine is much better when the addition of the impregnating agent is delayed for this period of time.

The improvement in the freeness of the resin-impregnated pulp after a short period of standing in contact with the cationic melamine resin is shown in Fig. 8 of the drawings, and the effect of varying conditions of acidity and alkalinity during this standing period are illustrated in Fig. 7. The results shown graphically in Fig. 7 were obtained by adding sufficient acid or alkali to a 1.5% aqueous suspension of bleached alpha pulp to produce the desired pH upon addition of a cationic melamine-formaldehyde-hydrochloric acid colloid, then adding the melamine resin colloid in amounts of 6% resin solids, based on the weight of the paper pulp, stirring thoroughly and allowing the suspension to stand overnight. The next morning the pH was adjusted to about 7.0 by adding acid or alkali and a dispersion of emulsion-polymerized polystyrene was added in amounts of 100%, based on the weight of the paper stock, and the freeness was determined on a Williams Freeness tester. This instrument is

a small sheet-making machine calibrated to permit measurement of the drainage time of the water through the paper-forming wire. The percent resin retention was determined by measuring the increase in weight of the dried sheet, and the values on the left-hand scales of Figs. 7 and 8 of the drawings represent:

$$\frac{\text{weight of dry sheet} - \text{weight of fiber added}}{\text{weight of resin added}} \times 100$$

It will be noted that maximum resin retention and lowest drainage time come at a pH of about 5, which is also a normal pH for papermaking. It will also be seen, however, that good retention is obtained over a wide range of pH values, which is another advantage of the invention.

The results shown graphically in Fig. 8 were obtained with the same quantities of polystyrene and paper pulp at 1.5% stock consistency, but using 10% of cationic melamine-formaldehyde resin-hydrochloric acid colloid. In this series of tests the melamine resin colloid was added to the paper stock suspension, the resulting pH being about 3.0, after which the stock was allowed to stand for varying periods of time before neutralizing with sodium hydroxide to a pH of 6-7 and adding the polystyrene dispersion. Drainage time was then determined on the Williams Freeness tester and resin retention was determined by measuring the weight of the dry sheet.

This curve shows that a reasonably low drainage time is obtainable with very high quantities of resin, in this case equal to the weight of the paper stock, after a standing time of only 30 minutes, and that even better results are obtained with a longer standing time up to 3-4 hours. No decrease in resin retention is noted when longer standing times are used.

After pretreatment of cellulosic stock with the cationic melamine resin, the impregnating agent is introduced in the form of an aqueous suspension, preferably of relatively fine particle size. Insofar as we have been able to determine, the flocculating action of the cationic melamine-aldehyde 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 melamine resin-treated cellulose fiber is quite rapid, and the standing time of the mixture after the impregnating agent has been added makes very little difference in the results obtained. The stock can therefore be formed immediately after the addition of the impregnating agent or after a considerable period of time, as desired.

The optimum quantity of the colloidal melamine 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 melamine resin colloid, the time of contact between the pulp fibers and the melamine resin colloid, 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 melamine resin colloid in order to obtain increased properties thereof in the finished product. In general, the proper amount of melamine 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. It is usually desirable to run trials with the specific dispersion to be added, under the desired operating conditions, before deciding finally on the exact proportions to use.

Thus, for example, one series of tests was made by adding increasing quantities of an aqueous dispersion of emulsion-polymerized polystyrene, prepared with the aid of an anionic emulsifying agent and having a particle size of less than 0.5 micron diameter, to suspensions of 3 g. of kraft paper pulp in 500 ml. of water to which 0.15 g. of colloidal melamine-formaldehyde resin had been added. It was found that in neutral solutions (pH=7) about 10 parts by weight of polystyrene were retained in a sheet of paper made from the above mixture for each part of melamine resin. When the pH of the stock prior to addition of the polystyrene dispersion was raised to 10 by the addition of an alkali such as ammonium or sodium hydroxide about 6 parts of the polystyrene were retained in the formed sheet, while stock adjusted to a pH of 4.0 with acid showed a retention in the finished sheet of about 14 parts of polystyrene for each part of colloidal melamine resin. These results show that although the pH of the stock has an appreciable effect on the retention of dispersions under some conditions, it is possible by suitable adjustments to retain large amounts of a resin or other dispersion in paper over a wide pH range of the stock. Additional examples will be presented later in which variations in pH show even less effect on the retention of resinous dispersions.

Another set of experiments was made at three different stock consistencies in which all conditions were held constant except the proportion of melamine resin colloid in the furnish. Two gram portions of moderately beaten alpha pulp were first treated with varying proportions of melamine resin colloid and the suspensions allowed to age at a pH of about 3-4 for about 15 hours. Then the suspensions were adjusted to a pH of 6.5-7.0 and two grams (dry basis) of an aqueous anionic dispersion of polystyrene were added with stirring. After standing for 5 minutes each batch of pulp and resins was filtered on a 60-mesh wire in the Williams Freeness tester noting the time for drainage, the clarity of the white water and the total weight and nitrogen content of the finished dry sheet. The results of these tests are shown graphically in Fig. 9 of the drawings, wherein the solid curves represent total resin retention (i. e. both polystyrene and melamine resin) while the broken lines show drainage time as indicated on the right-hand scale. It will be noted that the retention of resins increases rapidly up to a maximum of more than 80% when about 2-10% of melamine resin colloid, on the weight of the polystyrene, is used, the exact amount varying with the stock consistency. With increasing proportions of melamine resin colloid, the overall resin retention decreased to some extent. It also will be noted that the drainage time increases as the proportion of melamine resin colloid is increased. Since in most commercial operations it would be desirable to run with the highest possible resin retention and the lowest possible drainage time, it is apparent that the optimum

proportion of melamine resin colloid to obtain such results would be about 3-8% on the weight of polystyrene to be added. At the same time, a higher proportion of melamine resin can be incorporated in the finished sheet, if desired, without too much sacrifice in resin retention and stock freeness.

Fig. 10 shows the effect of varying the ratio of impregnating agent to paper stock. The procedure described in obtaining the values shown on Fig. 9 was followed, but varying quantities of emulsified wax were used. Equal quantities of a 1.5% water suspension of moderately beaten alpha pulp was treated with the indicated quantity of colloidal melamine-formaldehyde-hydrochloric acid colloid, allowed to stand overnight, neutralized with sodium hydroxide to a pH of 6-7 and the wax added as an aqueous emulsion of 50% solids, prepared with a lignin sulfonate emulsifying agent. The stock was then made up to constant volume, formed into paper on a hand-sheet machine, and the amount of wax was determined by solvent extraction.

These curves illustrate the fact that larger quantities of the cationic-melamine-aldehyde resin are needed to obtain the maximum retention with decreasing quantities of impregnating agent, but that 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 2-15%. 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 5-30% should be used. Larger quantities of the melamine resin colloid 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.

Although a high degree of flocculation and retention of the added impregnating agent is obtained by the use of cationic melamine-aldehyde resins alone, it is sometime advantageous to add an additional precipitating agent during the stock preparation. Thus, for example, better drainage of water from the stock on the papermaking wire or screen is frequently obtained when small quantities of alum on the order of 0.5-3%, based on the weight of the cellulosic material, are added. The alum or other precipitating agent is almost always added after the other ingredients have been mixed, since it would tend to coagulate and precipitate the colloidal cationic melamine resin in solution if it were added first, but in special cases where a preliminary coagulation of excess melamine resin may be desirable the alum or other electrolyte may of course be introduced ahead of the impregnating agent if desired.

The principles of our 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 applied to a more uniform incorporation of larger 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 these sizes 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 melamine-aldehyde 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 melamine resin takes place rapidly, and particles thereof, intimately mixed with the particles of colloidal melamine 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. Wall board, insulating board, and heavy stock for paper containers may be made by this method.

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 sheet 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 such as is used on a Yankee paper machine. By the use of our process cheaper and weaker pulps, such as ground wood, waste fibers, and short-fibered materials, may often be used while still obtaining good sheet properties.

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 stock is hydrated by heating 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 colloidal solution of cationic melamine-aldehyde resin is added in amounts of about 2-15% 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 alkali such as sodium or ammonium hydroxide to

the stock solution after the cationic melamine resin solution has been added but before introducing the resinous emulsion. Likewise alum may be added to assist in controlling the pH, eliminating foam or stickiness, and modifying the drainage 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 treated by our process 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 resistance. 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, and various thermosetting resins. Mineral fibers and fillers also may be incorporated at the same time to assist in obtaining maximum fire resistance.

PREFORMING AND MOULDING

Cellulosic fibrous materials such as paper stock impregnated with resinous binders by the process of our 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 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 of preforming or premoulding has been de-

veloped, 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 "white water" when operating in accordance with the principles of the present invention.

Preforms prepared with the aid of cationic melamine-aldehyde resin solutions have greatly simplified many moulding problems and have increased 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 melamine-aldehyde 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 25%, 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. Other resins, such as

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

Weighed samples of dry bleached kraft pulp were diluted to 1% consistency and 1,200 cc. portions were used to make handsheets treated as follows:

- A. No additions.
- B. 10% of colloidal melamine-formaldehyde resin was added, based on the dry weight of the pulp.
- C. 100% of emulsion-polymerized polystyrene was added, based on the dry weight of the pulp.
- D. 10% of the colloidal melamine-formaldehyde resin was added with stirring and then 100% of the polystyrene dispersion.

Handsheets were made by filtering 1,000 cc. portions of each pulp slurry through a 150-mesh copper screen in a Buchner funnel. The filtrate was returned through the residue two times. The volume of filtrate was then measured and the total solids determined. The sheet was dried, weighed and analyzed for total nitrogen.

The results are shown in the following table in which all the figures are by weight and are expressed in grams.

Process	Materials Added				Materials Found			
	Fiber ¹	HCl	Poly-styrene	Total	White Water Solids	Dry Sheet	Total	Melamine Resin in Sheet ²
A.....	6			6.0	0.08	6.19	6.27	
B.....	6	0.6		6.6	0.33	6.82	7.15	0.25
C.....	6		6.0	12.0	6.08	6.70	12.78	
D.....	6	0.6	6.0	12.6	0.25	13.52	13.77	0.53

¹ Approximate.

² Determined by Kjeldahl nitrogen analysis.

those described in the following examples, can also be applied.

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 a cylinder machine. Heavier board for moulding purposes is often made on a so-called "wet" machine; i. e. a papermaking 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

These results show clearly the increase in retention both of polystyrene and of cationic melamine-formaldehyde resin that is obtained when the two are used together. The untreated paper pulp failed to retain any appreciable amount of polystyrene, despite the fact that the white water was filtered twice. It retained only about 40% of the added melamine resin colloid when no polystyrene was used. However, substantially all the polystyrene (at least 95%) and approximately 90% of the melamine resin were retained in Process D wherein both ingredients were added.

The polystyrene used in this and other examples was prepared as follows: 1.2 parts by weight of "Duponol C" were dissolved in 58.8 parts of water heated to 94° C. and 0.05 part of 40% hydrogen peroxide were added. 40 parts of styrene were then introduced uniformly over 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 10.3% Na₂SO₄ and 3.4% moisture.

Example 2

A colloidal solution of cationic melamine-formaldehyde resin was prepared as described in U. S. Patent No. 2,345,543 by dissolving to a 12% solution a spray-dried condensation product of about 3 moles of aqueous formaldehyde solution with one mole of melamine in warm water containing 0.8 mole of HCl for each mole of melamine and aging about 16 hours.

Bleached kraft pulp was soaked in water for 1/2 hour, circulated in a five pound laboratory beater for 1/2 hour, beaten 1/2 hour under full load (31 lbs.), refined for 2 minutes in a laboratory Jordan and adjusted to 1.2% consistency.

A polyethylacrylate dispersion having a resin solids content of 25% and an average particle size less than 1 micron was prepared by the emulsion polymerization procedure described in Example 1, using the same emulsifying agent.

The paper stock suspension was first treated with 3% of colloidal melamine-formaldehyde resin, based on the dry weight of the fibers, by adding the resin solution and stirring for 30 minutes. The pH was then adjusted to about 6-7 by adding sodium or ammonium hydroxide and the polyethylacrylate emulsion was added. The mixture was then stirred 30 minutes and formed into sheets on a Valley handsheet machine having a 60-mesh forming wire. The sheets were couched from the wire with blotters and dried without pressing on a drum drier at 100-120° C. for approximately 10 minutes.

The retention of the acrylate emulsion was determined by examination of the white water. It was found that the melamine resin colloid was very effective in producing a uniform deposition and retention of the polyethylacrylate emulsion; in fact, the retention was practically complete in all cases. In the following table the figures in the column headed "Per cent acrylate" represent the percentage of polyethylacrylate solids added to the stock suspension, based on the dry weight of the paper fiber.

Sample No.		Per Cent Acrylate Added	Sheet Formation (Relative)	White Water	Weight, lbs./ream, 25" x 40" - 500
1.-----	Blank 1	-----	Good	Clear	147
2.-----	Control 2	5	do	Cloudy	-----
3.-----	do	10	do	Very cloudy	-----
4.-----	-----	0	do	Clear	-----
5.-----	-----	5	do	do	161
6.-----	-----	10	do	do	167
7.-----	-----	20	do	do	181
8.-----	-----	50	do	Sl. cloudy	197

¹ No melamine or acrylate resin.

² No melamine resin.

These results show that good retention of the polyethylacrylate by the cellulosic paper stock is obtained even when large quantities are applied.

Example 3

Bleached kraft paper pulp was soaked in water for 1/2 hour, circulated in a laboratory beater for 1/2 hour, and then beaten 1/2 hour with full load on the beater roll. The beaten pulp was refined for 2 minutes and diluted with water to 1.2% consistency. A quantity of colloidal melamine-formaldehyde resin equal to the dry weight of the paper pulp was added as a 12% solution acidified with 0.8 mole of hydrochloric acid per mole of melamine and the mixture was stirred 30 minutes. The pulp was then filtered and washed with a large quantity of water to remove all mel-

amine resin colloid not adsorbed by the pulp fibers.

The impregnated pulp was again suspended in water to 1% consistency, the suspension having a pH of 6.3, and one portion was made into handsheets, which were found on analysis to contain 1.1% of melamine resin. Another portion was treated with 100% of emulsion-polymerized polystyrene, based on the dry weight of the paper pulp, and handsheets were made. The same quantity of polystyrene emulsion was also added to another 1% slurry of the same paper pulp which had not been pretreated with the melamine resin and the same sheetmaking procedure was followed.

More than 80% of the polystyrene was retained by the melamine resin-treated pulp and was impregnated uniformly throughout the finished sheets. The sheets prepared from the untreated pulp contained little or none of the added polystyrene.

This example shows that the flocculating action of the colloidal melamine-aldehyde resins persists even after the resin has been adsorbed by fibrous materials. Cellulosic paper stock and other fibrous material pretreated with the resin colloid can therefore be used as a flocculating agent for emulsions or suspensions of waxes, gums, resins and other similar materials.

Example 4

A 12% solution of colloidal melamine-formaldehyde resin containing 5 grams of resin was diluted with water to 2 liters and 200 grams of an aqueous emulsion containing 50 grams of polystyrene were added with stirring. The polystyrene was immediately flocculated, and the resulting precipitate was filtered off. The filtrate was clear, showing that complete precipitation had been obtained.

The precipitated resin was dried, ground, and a portion was moulded at 155° C. and 3,600 pounds per square inch. A clear moulded piece was obtained.

A sample of the resin was analyzed for nitrogen and found to contain 6.75% of melamine-formaldehyde resin.

The above-described procedure was repeated using 25 grams of the melamine resin and 25 grams of polystyrene and neutralizing with ammonia prior to the filtration. A clear filtrate was again obtained. The precipitate contained 46% of melamine-formaldehyde resin.

This example shows the flocculating action of the colloidal, cationic melamine-aldehyde resin solutions in the absence of fibrous cellulose material and illustrates the importance of the presence of excess melamine resin colloid in the system over and above that which has been adsorbed on the cellulosic fibers. However, the coagulation of resinous dispersions in aqueous dispersions

containing no fibrous cellulosic material is not claimed as such in the present application, since this is claimed in our copending application Serial No. 604,967 filed concurrently herewith.

Example 5

80 parts by weight of dry bleached kraft pulp were mixed with water to a 1% suspension and 168 parts of a 12% colloidal cationic solution of melamine-formaldehyde resin (20% on the dry paper stock) were added and stirred for 10 minutes. The pH of the slurry was adjusted to 4.0 and 160 parts of an emulsion-polymerized polystyrene dispersion having a particle size of about 0.5 micron were added and the mixture stirred for an additional 10 minutes, after which it was diluted to 0.6% paper pulp and made into handsheets on a Valley machine. The white water was clear, indicating that substantially all the polystyrene was retained by the paper stock.

The handsheets were shredded mechanically, filled into a mold at 155° C. and pressed at that temperature for 5 minutes. A well-moulded piece of good mechanical strength and appearance was obtained.

A second batch of kraft pulp was impregnated with 20% of melamine-formaldehyde resin and 200% of polystyrene resin by the procedure described above, except the pH of the pulp slurry containing the cationic melamine-aldehyde resin was raised to 7.0 prior to adding the polystyrene dispersion. The impregnated pulp was formed into a sheet 0.25 inch thick on a Buchner funnel and dried at 200° F.

A disk was cut from the center of this sheet and placed in a disk mold at 155° C. After a few minutes for the preform to become heated the mold was closed and a pressure of 3600 lbs./sq. in. was applied for 5 minutes. The preform took

the shape of the mold without any apparent tearing, and a well-moulded piece of good appearance was obtained.

Example 6

A solution of 200 grams of a tertiary butyl phenol-formaldehyde condensation product in 300 grams of methyl cyclohexanone was mixed at 200° F. with 440 grams of water containing 2.5 grams of sodium dioctyl sulfosuccinate and 10 grams of a sorbitan monopalmitate-ethylene oxide condensation product. The mixture was homogenized to an emulsion having an average particle size of 1-2 microns. The solids content, as determined by heating a sample at 105° C. to constant weight, was 23.8%.

Bleached kraft paper stock was impregnated with the phenol-formaldehyde resin solution by the following procedure: The stock was diluted with water to 1% fiber consistency and colloidal melamine-aldehyde resin solution was added, the mixture stirred for 5 minutes, and the pH adjusted to the desired figure by the addition of sodium hydroxide or hydrochloric acid. The phenol-formaldehyde resin emulsion was then added, followed by an additional 5 minute stirring, whereupon the impregnated fibers were made into handsheets on a laboratory sheetmaking machine. These sheets were pressed between blotters and dried at 100-120° C. on a drum drier after which they were heated at 260° C. for one hour.

Various quantities of phenol-formaldehyde resin and melamine-formaldehyde colloid were applied to the stock in this manner and the resin retention was determined. The quantities used and the results obtained are given in the following table.

No.	Fiber ¹	Resin, Per Cent on Dry Fiber		pH of Slurry	Caliper (inches)	Ave. Sheet, Wt. (Grams)	Per Cent Resin Retention ²
		Phenol	Melamine				
A1-----	0.5	50	5	7.0	0.010	0.60	31
A2-----	1.0	50	5	7.0	0.017	1.29	53
A3-----	2.0	50	5	7.0	0.031	2.70	64
A4-----	3.0	50	5	7.0	0.046	4.34	81
B1-----	0.5	100	10	7.0	0.010	0.75	45
B2-----	1.0	100	10	7.0	0.018	1.61	56
B3-----	2.0	100	10	7.0	0.032	3.36	62
B4-----	3.0	100	10	7.0	0.049	5.38	72
C1-----	0.5	150	15	7.0	0.012	0.94	53
C2-----	1.0	150	15	7.0	0.022	2.00	61
C3-----	2.0	150	15	7.0	0.042	4.30	70
C4-----	3.0	150	15	7.0	0.063	6.91	79
D1-----	0.5	200	20	7.0	0.012	1.01	46
D2-----	1.0	200	20	7.0	0.025	2.38	63
D3-----	2.0	200	20	7.0	0.049	5.22	73
D4-----	3.0	200	20	7.0	0.070	8.92	90
E1-----	0.5	150	15	4.0	0.009	0.62	14
E2-----	1.0	150	15	4.0	0.017	1.37	22
E3-----	2.0	150	15	4.0	0.032	2.89	27
E4-----	3.0	150	15	4.0	0.049	4.63	33
F1-----	0.5	150	15	5.0	0.010	0.82	39
F2-----	1.0	150	15	5.0	0.022	1.86	52
F3-----	2.0	150	15	5.0	0.041	3.99	60
F4-----	3.0	150	15	5.0	0.061	6.55	72
G1-----	0.5	150	15	6.0	0.011	0.88	46
G2-----	1.0	150	15	6.0	0.022	1.97	59
G3-----	2.0	150	15	6.0	0.043	4.27	69
G4-----	3.0	150	15	6.0	0.060	6.76	76
Blank-----	0.5	None	None	7.0	0.009	0.53	-----
Do-----	1.0	None	None	7.0	0.016	1.05	-----
Do-----	2.0	None	None	7.0	0.026	2.06	-----
Do-----	3.0	None	None	7.0	0.035	3.16	-----

¹ Grams of dry fiber in the suspension from which the sheet was made.

² Sheet weight—Fiber Weight of resin added × 100.

These results show that a high degree of retention of thermosetting resins of the type of phenol-formaldehyde condensation products is obtained by the use of colloidal melamine-aldehyde resin solutions. Other phenol-formaldehyde condensation products, such as those prepared from phenol itself, mixtures of phenol and cresols, and mixtures of phenol, cresols and xylenols may also be used.

Modified phenolic resins may also be applied to fibers of cellulose and the like by the use of colloidal melamine-formaldehyde resin solutions as illustrated in this example. Thus, for example, resins obtained by the condensation of mixtures of phenols and aminotriazines such as melamine with formaldehyde or other reactive aldehydes may be applied in this manner. Typical aminotriazine-phenol-formaldehyde resin syrups that may be used are described in detail in U. S. Patent No. 2,229,291. Any of these resins may be emulsified and applied to aqueous suspensions of a filler such as paper stock by the procedure described above, and the resulting impregnated filler is well suited for use in pulp moulding processes.

Example 7

Sheets impregnated with phenol-formaldehyde resin by the process described in the preceding example were moulded into laminated board. A water suspension of bleached kraft stock of 1% consistency was treated with 20% of melamine-formaldehyde resin colloid and then with 200% of the phenolic resin, based on the dry weight of the paper fibers, and the resulting impregnated stock was made into 6 x 6-inch sheets on a Valley handsheet machine. The wet sheets were pressed between blotters, dried on a drum drier at 100-120° C. and then heated in an oven at 260° F. for 1 hour. The dry sheets contained about 60-70% resins.

Laminations were made by superimposing 3 to 6 sheets and pressing between 6-inch stainless steel platens at 3000 lbs./sq. in. at 160° C. for 10 minutes, followed by cooling under pressure. The resulting laminates had appreciable rigidity and a uniform translucency, indicating a uniform resin distribution.

Example 8

Kraft paper stock was impregnated with finely divided polystyrene and made into paper on a Fourdrinier papermaking machine. The stock was beaten at 6% consistency for 1.25 hours and then diluted with water to 2%. Colloidal cationic melamine-formaldehyde resin, acidified with 0.8 mol of hydrochloric acid per mol of melamine and aged 16-20 hours at 12% resin solids was added to the diluted stock in the beater chest with thorough agitation. After about 90 minutes sufficient sodium hydroxide solution was added to raise the pH to 6.7 and the polystyrene was then stirred in. An emulsion-polymerized polystyrene was used which was prepared by introducing styrene with agitation into a 2% water solution of "Duponol C," a sodium alkyl sulfate emulsifying agent, heated to 95° C, adding 5-8% hydrogen peroxide, refluxing to complete the polymerization, diluting to 30% solids and steaming to remove unreacted monomer, and diluting to 24.3% solids.

After all the resin was added the stock consistency was 2.57%. On the dry basis the furnish contained 62.8% pulp, 33.7% polystyrene and 3.5% melamine-formaldehyde resin. The stock was not further refined after its original

beating. The purpose of the run was to make 10-point (0.010-inch) laminating paper, and it was found that this caliper was obtained at a consistency in the head box of 0.91% solids and a wire speed of 27 feet per minute. At first the stock was run out on the machine at 20° C., but at this temperature it was quite slow on the wire. Much better performance was obtained by heating the stock to 35° C. With this change, and with a few adjustments to the suction at the boxes and couch roll to prevent sticking on the first press roll the machine was operated successfully.

During the last part of the run alum in amounts of 1-2% on the weight of the fiber was added at the beater chest and in the closed white water system. This made the stock slightly more free on the papermaking wire.

The machine was equipped with 17 drying rolls which were operated at temperatures increasing from 100° F. at the first drier to 188° F. at the last. There was no deposit on or sticking to the drier felts, and no deposit on the driers. The finished sheet contained 74.6% paper fibers, 22.6% polystyrene and 2.8% melamine-formaldehyde resin. The resin retentions were therefore 57% and 68%, respectively. Only 0.06% of chloride ion was present, thus showing that all the hydrochloric acid was released from the cationic melamine resin during the process.

A sample of the resin-impregnated paper made in this run was broken up by continued beating in water, dried, and an electron photomicrograph made of a representative sample of the fibers at 14,000 diameters. This photomicrograph is reproduced as Fig. 5 of the drawings. Reference to this figure shows the adhesion of the flocculated resin to the individual cellulosic fibers.

Example 9

Two additional mill trials were made on the papermaking machine referred to in the preceding example using the same polystyrene emulsion and cationic melamine-formaldehyde resin in larger quantities.

In the first of these runs the furnish contained, on the dry basis, 48.1% of bleached kraft paper pulp, 47.1% polystyrene and 4.8% of the melamine-formaldehyde resin. The stock was prepared as described in the preceding example, no alum being added, at a consistency in the stuff box of 3.63% and a pH of 4.5. At the head box the consistency was 0.81%, the stock temperature was 34-47° C., and the pH was 6.2. (The water supply was slightly alkaline, having a pH of 8.2.) Paper having a caliper of 12-16 point (0.012-0.016 inch) was made without difficulty at a wire speed of 28.5 feet per minute using drying roll temperatures of from 110° to 195° F. The paper analyzed 55.5% cellulose pulp, 40.3% polystyrene and 4.2% melamine-formaldehyde resin and the retentions were therefore 74% of the polystyrene and 75% of the melamine resin. Even larger quantities of resins were incorporated into the paper during the second run. The furnish contained on the dry basis 35.4% kraft pulp, 58.9% polystyrene and 5.7% cationic melamine-formaldehyde resin. The machine speed was 28.3 feet per minute, as before, and the paper was 0.012 inch in thickness and contained 50.6% pulp, 44.5% polystyrene and 4.9% melamine resin. The paper from both runs had a very low chlorine content (0.05%).

Fig. 6 of the drawings is a photomicrograph of fibers of the paper containing 44.5% poly-

styrene and 4.9% melamine resin. This figure shows clearly that at high resin-pulp ratios the individual fibers are completely coated with resin, yet retain their identity as fibers and thus their sheet-forming characteristics. The location of the resin along the individual fibers in Figs. 5 and 6 demonstrates clearly the unusual flocculating properties of the cationic melamine aldehyde resins.

What we claim is:

1. 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 colloidal solution of hydrophilic cationic melamine-aldehyde resin to the aqueous fiber suspension, then adding an aqueous dispersion containing the impregnating agent in deflocculated condition and flocculating the impregnating agent in admixture with the suspended fibers by the action of the cationic melamine-aldehyde resin, and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibers along with melamine-aldehyde resin.

2. A method according to claim 1 in which the quantity of water-insoluble hydrophobic organic impregnating agent is more than 5% but not more than about 200% of the dry weight of the fibrous cellulosic material.

3. A method according to claim 1 in which the water-insoluble hydrophobic organic impregnating agent comprises polystyrene.

4. A method according to claim 1 in which the aqueous dispersion of deflocculated impregnating agent contains a member of the group consisting of anionic and nonionic emulsifying agents.

5. 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 melamine-aldehyde resin in amounts of 2-30% of the weight of the organic impregnating agent to be added, allowing the suspension to stand at a pH in the range of about 2.5 to about 7.0 for at least 30 minutes, then adding an aqueous dispersion containing the hydrophobic organic impregnating agent in deflocculated condition, flocculating the impregnating agent in admixture with the suspended cellulosic fibers by the action of the cationic melamine-aldehyde resin, and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibers along with melamine-aldehyde resin.

6. A method according to claim 5 in which the quantity of water-insoluble hydrophobic organic impregnating agent is more than 5% but not more than about 200% of the dry weight of the fibrous cellulosic material.

7. A method according to claim 5 in which the water-insoluble hydrophobic organic impregnating agent comprises polystyrene.

8. A method for the production of felted fibrous cellulosic material having a uniform content of a water-insoluble hydrophobic organic impregnating agent which consists in preparing a

water suspension of the fibrous cellulosic material, adding to said suspension a colloidal solution of hydrophilic cationic melamine-aldehyde resin, allowing the resulting suspension to stand at a pH of about 3-6 for at least 30 minutes, neutralizing the suspension by the addition of alkali, and then adding an aqueous dispersion containing the water-insoluble hydrophobic organic impregnating agent in a deflocculated condition, flocculating the impregnating agent in admixture with the suspended fibers by the action of the cationic melamine-aldehyde resin and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibers along with melamine-aldehyde resin, and forming the impregnated fibers into a felted product while draining the suspending water therefrom.

9. A method according to claim 8 in which the quantity of water-insoluble hydrophobic organic impregnating agent is more than 5% but not more than about 200% of the dry weight of the fibrous cellulosic material.

10. A method according to claim 8 in which the quantity of water-insoluble hydrophobic organic impregnating agent is about 50-100% of the dry weight of the fibrous cellulosic material and the quantity of hydrophilic cationic melamine-aldehyde resin is about 2-15% of the weight of said hydrophobic organic impregnating agent.

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