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, pitch, bitumens, oils, etc., into fibrous cellulosic material such as paper stock, cotton, and the like, followed if desired by forming the resulting pre-treated cellulosic material into fibrous felted sheets or articles such as paper, paperboard, molded or premolded cellulosic articles and the like. The invention includes processes for the manufacture of new types of paper, paperboard, pulp and pulp preforms as well as a wide variety of products obtained therefrom, either directly or by subsequent treatments such as drying, 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 resin soap, resin or wax emulsions or dispersions, lattices, 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 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, dryers, 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. Water drainage often becomes too slow for sheet formation.

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

7. Agglomerates of the resin, together with unprefecitated resin, tend to deposit as sticky aggregates in pipe lines, tanks, and various other portions of the paper-making equipment.

Some of these difficulties, such as the appearance of resin 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 resin 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 paper-making or pulp-forming or performing 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 suc-
cessfully 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 premolding and molding processes.

Similarly, a wide variety of organic binders, sizing agents, oils, waxes, pitches, gums and natural resins may be incorporated into fibrous cellulosic materials. Various combinations of any two or more of these materials may likewise be incorporated if desired. By applying the principles of this invention, resin-impregnated paper or paperboard having superior properties can be prepared, as well as new types of products made from the treated paper of pulp by such conventional operations as laminating, molding, pressing, calendaring, extruding and the like. Instead of forming the treated pulp or fibers, they can be shredded, chopped or ground to produce new types of insulating agents, molding powders, fillers for standard molding 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 urea-formaldehyde 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 urea-formaldehyde resin causes a controlled flocculation such that the particles of the impregnating agent are uniformly coated or impregnated into the cellulose fibers. When dispersed or deflocculated water-insoluble impregnating or coating agents are applied in this manner, 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 urea-formaldehyde 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 urea-formaldehyde 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 dispersion 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 distinctive flocculating action of the cationic urea-formaldehyde resin, and is in many instances actually enhanced, after the cationic resin has been absorbed on the fibrous cellulosic material. The importance of this discovery resides in the fact that the cationic resin, being distributed over and through the cellulose fibers, causes a uniform dispersion and retention of the impregnating agent on the fibers after it has been flocculated. Large quantities of any desired impregnating agent may therefore be deposited on fibrous cellulosic materials such as paper stock while retaining the felting properties of the fiber. So that after impregnation they can still be felted together and formed into sheeted or molded products by conventional wet-molding or paper-making procedures.

Although the invention is not dependent on any particular theory of operation, the following is offered as the most satisfactory explanation of the unusual type of flocculation and retention that is obtained. As is noted above, definite quantities of the cationic urea-formaldehyde resin are adsorbed upon and retained by the cellulose 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 cellulose pulp, the dispersed particles are flocculated on the positively charged fibers forming a 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.

The cationic urea-formaldehyde resins which are employed in the process of our invention are prepared by condensing a urea-formaldehyde reaction product under acid conditions, and preferably at pH values below 4.0-4.5, in the presence of a cationic nitrogen-containing organic compound which is capable of condensing with the resin. The preferred cationic organic nitrogen compounds which are capable of condensing with dimethyolurea or other urea-formaldehyde reaction products are water-soluble polyfunctional organic nitrogen bases; i.e., compounds having the ability to copolymerize with urea-formaldehyde under acid conditions. Typical examples of such polyfunctional organic bases are the alkylenepolyamines of the formula:

\[ \text{H}N(C\text{H}_2\text{HN})\text{H} \]

in which \( x \) is one or more, such as ethylenediamine, 1,3-propylenediamine diethylenetriamine, triethylenetetramine, tetraethylenepentamine, the corresponding polypolyaliphaticamines and polybutylenopolyamines, also guanidines, biguanides, condensation products of alkylenepolymers (such as those above) and compounds such as alpha-dichlorhydrin, epichlorhydrin and the like, monoalkyloalamines, dialkyloalamines and the like, and the water-soluble condensation products thereof with aldehydes such as formaldehyde. By condensing these and similar polyfunctional cationic organic bases with dimethyolurea and similar primary or substantially monomeric urea-formaldehyde condensation
products, obtained under slightly alkaline conditions by condensing urea or thiourea with formaldehyde, in the presence of sufficient acid to reduce the pH to values of about 1.0 to 4.0, and preferably to about 1.0 to 2.5, measured after the reaction has proceeded for some time, there are obtained cationic urea-formaldehyde resins which are substantive toward cellulose materials and can be used in the process of our invention.

The cationic urea-formaldehyde resins employed in practicing the present invention are therefore prepared by first reacting urea with a methylene-yielding substance such as formaldehyde, paraformaldehyde, or hexamethylenetramine in known manner to form a primary urea-formaldehyde condensation product which is usually designated by resin chemists as dimethyloleurea. This primary reaction product is preferably formed under neutral or slightly alkaline conditions, the latter being obtainable by the addition of a small quantity of basic material such as sodium hydroxide or triethanolamine. A suitable quantity of the polyfunctional organic base is then added as such or after it has first been reacted with formaldehyde and the resin solution is acidified by the addition of hydrochloric acid, nitric acid or other strongly acidic material to reduce the pH to the polymerizing range, which is about 1-4 and preferably 1-2. The resin syrup is then further reacted or polymerized, preferably at elevated temperatures on the order of 70°-90° C., in order to bring about a polymerization or copolymerization of the urea-formaldehyde and organic base and thereby produce a cationic resin.

The relative proportions of polycroloalkylene polyamine and primary urea-formaldehyde condensation product may be varied over a wide range. This is an important advantage of the invention, since it permits an adjustment of the degree of cationic properties of the resin for emulsions of widely divergent characteristics including, for example, those containing anionic or non-ionic emulsifying agents. Thus for some purposes it may be most desirable to employ a resin prepared from 10% by weight of a polycroloalkylene polyamine and 90% of urea-formaldehyde condensation product, while for other purposes a cationic resin containing considerably more of the polycroloalkylene polyamine may give better results. Cationic resins prepared from as much as 80% by weight of a polycroloalkylene polyamine such as tetracroloalkylene-pentamine and 20% by weight of the primary urea-formaldehyde condensation product may be used in cases where rapid curing of the resin is not important.

The polymerized resin syrup is preferably neutralized to a pH on the order of about 6-7 in order to obtain a product which is stable on storage. Resin syrups prepared by this method are both water-soluble and water dilutable, and also can be evaporated to dryness and redissolved in water without substantial reduction in their water solubility.

The process of the invention may thus be used to apply any water-insoluble coating or impregnating agent in amounts varying from a few percent up to more than the weight of the fibrous cellulose material. By "coating" or impregnating agent we mean, of course, a material which will coat or impregnate the cellulose 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 which may be applied:

Waxes
Paraffin
Petrolatum
Crude scale wax
Microcrystalline or amorphous petroleum wax
Carnauba wax
Chlorinated waxes
Montan wax

Bituminous
Asphalt
Bitumens
Tars and pitches
Wood resin
Hydrogenated resin
Gum resin
Limed resin
Heat-treated resin
Sulfur-treated resin
Disproportionated resin

Elastomers
Natural latices
Butadiene polymers
Synthetic latices
Copolymers of butadiene, isoprene, etc.
Isoprene polymers
Acrylic polymers
Neoprene polymers
With acrylonitrile

Resins—thermosetting
Phenol-aldehyde resins including particularly the phenol and alkyl phenol formaldehyde molding resins
Lignin-phenol-formaldehyde resin dispersions (U. S. Patent No. 2,387,090)
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
Polyethylene
Polystyrene
Polyacrylates
Polymethacrylates
Polyvinyl esters such as vinyl chlorides and vinyl acetate polymers and copolymers of the two
Polyvinyl acetel
Polyvinyl alcohol
Copolymer of styrene with vinyl chloride, acrylate acid esters, acrylonitrile, etc.
Thermoplastic phenol-formaldehyde resins, including phenol-acetaledehyde and phenol-furfural resins and corresponding resins obtained from cresols and other alkyl phenols
Oil-modified phenol-formaldehyde resins
Esters of resin with polyhydric alcohols such as glycerine, pentaerythritol, dipentaerythritol, polyglycol alcohols, etc.
Polyindene resins
Cumarone resins
Vinylacetene resins
Vinylresin resins
"Vinyl" resin; i. e. residue from purified wood rosin
Halogenated vinylacetene resins
Acetyl gums

Any of the above materials, either singly or in admixture, may be applied to fibrous cellulose
materials with the aid of cationic urea-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 lattices. 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 cycloaliphatic acids such as potassium oleate, potassium naphthenate and the like, amine salts 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 naphthalene sulfonate, sodium isopropyl naphthalene sulfonate, esters of sulfo-carboxylic acids such as esters of sodium sulfo-acetate, dialkyl sulfo-succinates, disodium monoalkyl sulfo-succinates; amides of sulfo-carboxylic acids such as sodium sulfo-succinamates and the like, sulfonated lignin, etc.

Ammonium or other water-soluble or water-dispersable salts of alkyl 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, polyhydroxy 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 cellulose material capable of adsorbing cationic urea-formaldehyde resin from an aqueous dispersion thereof may be coated or impregnated by the process of the invention. A wide variety of fibrous cellulose material used in the preparation of paper, board, molded resin fillers and the like may be used, such as kraft pulp, rag pulp, soda, sulfate, groundwood, sulfate 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 cellulose or non-cellulosic, that may improve the impact resistance, mechanical strength or other properties of the formed or molded 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, molded articles, preformed articles, electrical insulators, heat-insulating paper, or loose masses of unfelted and unmolded 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 cellulose material may vary somewhat with different impregnating agents, but generally follows the same general plan. The cellulose 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 device if desired. Any desired ratio of cellulose material to water may be maintained but we prefer to operate at a stock consistency of about 0.5% to 6%. The cationic urea-formaldehyde resin is then added, preferably in the form of an aqueous solution 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 aging 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 paper-making 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 urea-formaldehyde resin and prior to addition of the impregnating agent should preferably be within the range of from about 1 to about 6 since the resin retention is not as good at higher or lower values.

After pretreatment of the cellulose fibers with the cationic urea-formaldehyde 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 urea-formaldehyde-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 paper-making 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 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 cationic urea-formaldehyde 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, the time of contact between the pulp fibers and the cationic 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 urea-formaldehyde resin in order to obtain increased properties thereof in the finished product. In general, the proper amount of urea-formaldehyde resin required may vary from small amounts on the order of 1%, based on the weight of the paper stock, up to about 15% or more. When using relatively large quantities of impregnating agent, on the order of 50%-100% or more of the weight of the cellulose fibers, the optimum quantity of cationic resin is within the range of about 1%-10%, 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 should be used. Larger quantities of the modified urea-formaldehyde 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 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 upon the exact proportions of cationic urea-formaldehyde resin to use.

The principles of the invention may be applied in a wide variety of fields of paper making, molding, laminating, extruding, preforming and the like and in general wherever a fibrous cellulosic material intimately associated with thermoplastic, thermostetting, waxy, bituminous or other type of bonding, impregnating or coating material is desired.

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

A solution of 271.2 grams of 37% formaldehyde and 80 grams of urea was adjusted to a pH of 8.8-8.8 with triethanolamine, and the mixture was then added to the mixture, together with 12 grams of water, and after slight cooling, 12 grams of commercial hydrochloric acid diluted with an equal amount of water was added to the mixture. The temperature of the mixture was brought to 70°C. and maintained at this point for 1 hour. Thereafter the cooled viscous syrup was neutralized with 10% sodium hydroxide, under which conditions the resin remained stable.

Bleached kraft pulp, at a Green freeness of 475 and approximately 1.5% consistency was treated with various amounts of the above resin, as set forth in the table below, and allowed to stand for several hours at a pH of 4.0-5.0. The stirringly was then adjusted to a pH of 6.5 with dilute sodium hydroxide and a polystyrene emulsion equivalent to 100% on polystyrene solids, of the dry fiber weight was added to the 70 slurry which was then stirred for 15-30 minutes. Thereafter, the slurry was diluted to 1% fiber consistency. Handsheets were then made on a Williams freedom tester employing approximately 200 cc. of the fiber-resin suspension for each sheet. The sheets were dried to constant weight at about 100°C. The polystyrene used in this and the other illustrative examples was prepared as follows: 1.2 parts by weight of sodium lauryl sulfate were dissolved in 58.8 parts of water heated to 94°C. and 0.03 part of 40% hydrogen peroxide were added. 40 parts of styrene were then introduced uniformly over a 1.5 hour, with agitation sufficient to cause emulsification thereof. The exothermic polymerization reaction proceeded smoothly and was complete after 3.5 hours. Steam was blown through the batch to remove any remaining material and the dispersion was adjusted to 25% solids.

Example 2

33.75 grams of urea and 142 grams of 37% formaldehyde solution were reacted under slightly alkaline conditions for 15 minutes at 70°C. Following this reaction period, 23.75 grams of tetraethylenepentamine and sufficient concentrated hydrochloric acid were added to give a pH of about 3 and the condensation was continued by heating at 70°C. for an additional 1½ hour.

Example 3

A resin syrup was prepared in the same way as in Example 2 employing 11.25 grams of urea, 191 grams of 37% formaldehyde solution and 47 grams of tetraethylenepentamine.

Example 4

A solution of 18.9 grams of tetraethylenepentamine in 40 ml. of water was partially neutralized by the slow addition of 8 ml. of concentrated hydrochloric acid. The mixture was then cooled and to the amine solution was added slowly a cooled solution of 6.6 grams of acetaldehyde and 24.3 ml. of 37% formaldehyde. A viscous resin formed as a result of the strongly exothermic reaction. It was diluted with water to make a stable solution of 5% solids content.

Example 5

649 grams of an aqueous 37% formaldehyde solution was mixed with 16 ml. of 50% triethanolamine to adjust the pH of the solution to 8.3. 120 grams of urea were then added and the solution heated to 70°C. at which point it was maintained for 15 minutes. 130 grams of guanidine hydrochloride were added, followed by the addition of 15 ml. of 18.4% hydrochloric acid. The reaction was carried out at 70°-75° C. for 2½ hours and then at 96°-97° C. for 30 minutes. Thereafter the solution was cooled and neutralized with dilute sodium hydroxide solution.

Example 6

60 grams of urea were dissolved in 202 grams of 37% formaldehyde solution and the pH was adjusted to 8.5 by the addition of sodium hydroxide solution. The mixture was heated at 70°C. for 15 minutes and thereafter 1 ml. of concentrated hydrochloric acid was added, followed by the addition of 24 grams of ethanolamine added as the hydrochloride. The mixture was heated at 70°C. for 1 hour and the reaction mixture was thereafter neutralized with sodium hydroxide solution.

The above described resins of Examples 2-6 were employed as precipitants for polystyrene resin on bleached kraft pulp according to the
procedure set forth in Example 1. The results are given in the following table.

<table>
<thead>
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<th>Cationic Resin</th>
<th>Amount of Cationic Resin (Per Cent on Dry Fiber)</th>
<th>Drainage Time (Seconds)</th>
<th>Per Cent Retention of Polymeric Resin</th>
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<tr>
<td>Blank</td>
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<td>26</td>
<td>0</td>
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<td>Resin 1</td>
<td>1</td>
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<td>Resin 2</td>
<td>2</td>
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<td>Resin 8</td>
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<tr>
<td>Resin 10</td>
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What we claim is:
1. 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 finished product, the improvement which consists in first adding a partially polymerized hydrophilic cationic urea-formaldehyde-polyfunctional organic nitrogen base resin to the aqueous fibrous suspension, said cationic resin being formed by the condensation of a urea-formaldehyde reaction product with a water-soluble polyfunctional organic nitrogen base under acid conditions, then adding an aqueous dispersion of the organic impregnating agent in deflocculated condition and thereby immediately flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic urea-formaldehyde-polyfunctional organic nitrogen base resin, and thereby depositing a substantial proportion of the impregnating agent uniformly on the fibers.

2. A method of impregnating fibrous cellulosic material with an organic impregnating agent while preserving the freeness and felting properties thereof which consists in preparing a water suspension of the fibrous cellulosic material at 0.5–9% consistency, adding to said suspension a partially polymerized hydrophilic cationic urea-formaldehyde-polyfunctional organic nitrogen base resin in amounts of about 1%–5% of the weight of the fibrous cellulosic material, said cationic resin being formed by the condensation of a urea-formaldehyde reaction product with a water-soluble polyfunctional organic nitrogen base under acid conditions, aging the suspension in a non-alkaline condition for at least 30 minutes, then adding the requisite quantities of an aqueous dispersion of the organic impregnating agent in deflocculated condition, thereby immediately flocculating the impregnating agent in the cellulosic fibrous suspension by the action of the cationic urea-formaldehyde-polyfunctional organic nitrogen base resin, and thereby depositing 50–100% by weight of the impregnating agent on said fibers.

4. A method according to claim 1 in which the hydrophobic organic impregnating agent is a polystyrene resin.

What we claim is:

What we claim is:

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The following references are of record in the file of this patent:

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