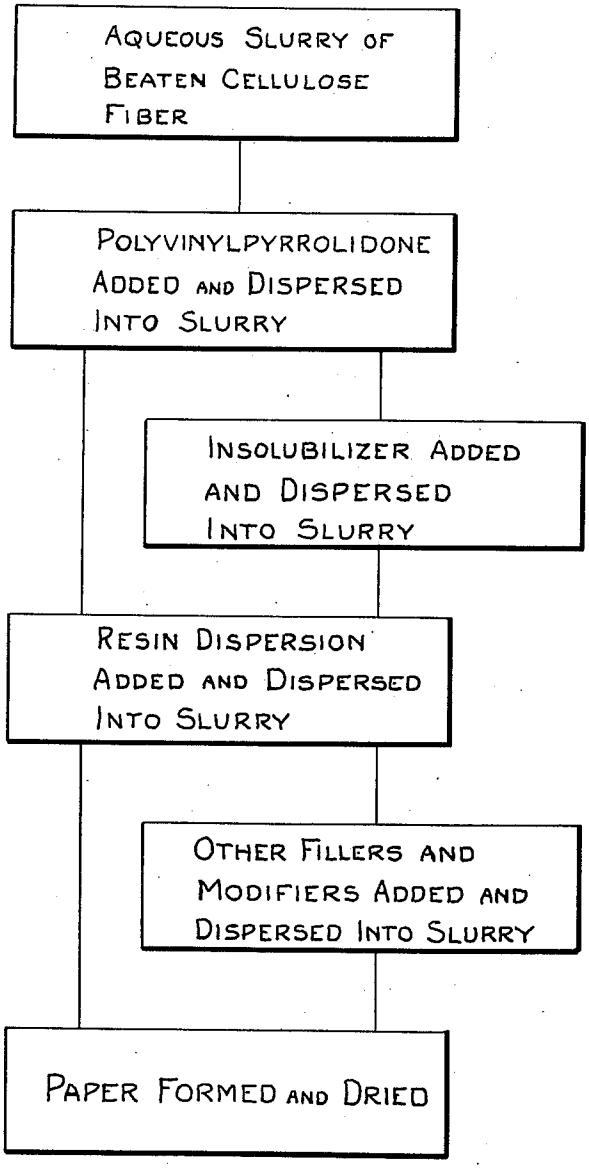
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PROCESS FOR INCORPORATING RESINS INTO PAPER

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PROCESS FOR INCORPORATING RESINS INTO PAPER

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This invention relates to the art of paper making, and more particularly refers to a novel method for incorporating resins and other additive materials into papermaking pulps at that point of the paper making process generally termed as the "wet end," and to the novel products produced thereby.

Unmodified paper and paper board made by conventional methods have many limitations. The products are weak, permeable to water, oil and grease, and lack many of the properties generally desired in a finished paper product. To improve its properties, modifying or reinforcing materials such as resins, pigments, fillers and other related materials are customarily added to the paper.

The majority of processes currently used for incorporating these materials into paper may be characterized as secondary operations, that is, they are methods for treating the paper after the paper itself has been fabricated. Such secondary operations, or applications of the modifying materials made to the basic paper, usually from solvent or hot-melt systems, succeed at best only in applying a film of the modifying material on the paper surface, and filling the interstices, but do not succeed in causing the fillers to penetrate the fibers themselves, since the fibers and additives are electrically repellent to each other. As a result, the full benefit of the modifying agent is not realized. Moreover, the addition of a separate treating step adds to the cost of processing. Even where wet-end processes have been used, complete retention of the additive by the pulp has not been achieved, with the result that the excess additive is generally removed in the form of unattached particles, which, together with the "fines" from the process, frequently cloud the water and render it nonreusable.

It is an object of the present invention to provide a process for the incorporation of resins and other modifying materials in an aqueous medium into papermaking pulp in the wet-end stage of the paper making process.

It is a further object to provide such a process wherein the resins and other additives are removed from the aqueous medium in which they are applied, and are tenaciously deposited upon the individual pulp fibers.

It is still further an object to provide such a process wherein modified papers are produced in which the modifying substance is uniformly dispersed throughout the paper.

It is a further object to provide modified paper materials which, while having the same modifying agent or additive content, exhibit greatly enhanced properties over products made by other methods.

It is a further object to provide various useful modified paper products produced by the methods of the present invention.

Other objects and advantages of the present invention will become apparent from the description which follows, and from the appended claims.

According to the present invention, polvinylpyrrolidone in aqueous solution is added and thoroughly mixed into an aqueous slurry of papermaking pulp which has been first beaten in the usual manner. The polyvinylpyrrolidone is adsorbed on the surface of the pulp fiber and functions as a coupling agent for the attachment of modifying resins and other additaments. The modifying materials are of such nature that they may be provided in

the form of an aqueous dispersion such as a suspension, colloidal solution, or true solution. When they are added to the polyvinylpyrrolidone-treated pulp slurry they are drawn to and are caused to be deposited uniformly on the treated pulp. The modified pulp furnish may then be processed in a normal manner to produce the finished paper or board end product.

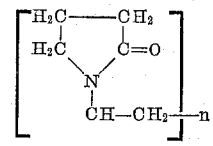
The drawing contains a flow diagram of the process of the invention.

A further improvement may be realized by adding an acidic insolubilizing agent to the slurry containing the polyvinylpyrrolidone-treated pulp, and thoroughly mixing the slurry. The insolubilizing agent aids in setting or insolubilizing of the polyvinylpyrrolidone, and enhances the coupling action of the polyvinylpyrrolidone between the pulp and the subsequently added resin. The preferred material is the linear copolymer of methylvinylether and maleic anhydride, or the half amide thereof.

The incorporation of a resin during the paper making process has several attractive potentialities. Because the addition is accomplished during the making of the paper, the additional steps of coating or impregnating of the finished paper and its attendant cost is avoided. Moreover, because the resin is incorporated while the fibers are separated, an extremely uniform dispersion of the resin about the fibers can result. It has been attempted in the past to provide a process wherein a resin introduced in an aqueous media in a paper beater would be absorbed by the pulp, leaving clear water substantially free from resin. However, these efforts have not been successful in view of the fact that only a small portion of the resin has been retained in the final paper, while the major proportion thereof has been lost when the water is removed during the paper making process.

The present process is dependent upon the discovery that when an aqueous solution of polyvinylpyrrolidone is introduced into a pulp slurry which has been adequately beaten it becomes deposited on the cellulose fibers and strongly attached thereto. The exact nature of the reaction or mechanism responsible for this phenomenon is not fully known. It is believed that the functional group of the polyvinylpyrrolidone reacts with the functional group of the cellulose molecules to form a bond in the nature of that of an addition compound. In actual practice, the polyvinylpyrrolidone migrates to the cellulose fibers and becomes firmly attached thereon. When an additive material such as a phenolic resin in aqueous dispersion is subsequently introduced into the slurry, it is believed that a similar reaction takes place between a functional group of the resin molecule and a functional group of the polyvinylpyrrolidone. The polyvinylpyrrolidone in effect becomes a cross-linking or coupling agent for the cellulose-resin system. This phenomenon can be easily observed, since, immediately after the addition of the aqueous resin dispersion or other modifying agent into the polyvinylpyrrolidone-treated pulp slurry, substantially all of it is removed from the aqueous solution and deposited on the pulp fibers, leaving the water clear. In fact, so pure is the water that it may be reused in the paper making process without further purification.

Polyvinylpyrrolidone is an acetylene derivative manufactured by the so-called "Reppe" high pressure and temperature technique. It is a water-soluble homopolymer of N-vinylpyrrolidone, having the following structure:

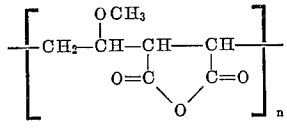


Polyvinylpyrrolidone is a white, free-flowing powder

having infinite solubility in water. It is presently commercially available in molecular weights of 40,000, 160,000 and 360,000. The polymers having the lowest molecular weight are preferred since they require less water for dilution. In the interests of convenience, polyvinylpyrrolidone will hereafter in the specification be referred to as PVP, its customary abbreviation.

PVP acts somewhat like a complexing agent and will combine with various materials which are used as modifying agents for the pulp, resulting in the formation of homogeneous mixtures. The most important of these are resins. In addition to resins, other additive materials may be incorporated such as pigments or fillers, synthetic fibers such as acrylic, polyester, and polyamide fibers, and inorganic fibers and flakes such as glass, mica, silica, asbestos, metallic powder, and other related materials.

The copolymer of vinylmethylether and maleic anhydride, which will hereafter in the specification in the interests of convenience be designated by its customary abbreviation as PVM/MA, is a linear copolymer consisting of alternating vinylmethylether and maleic anhydride units, and has the following general structure:

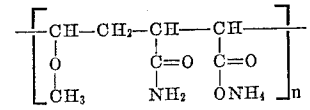


PVM/MA is a white amorphous powder having infinite solubility in water. Its water solutions are highly polar. According to the invention, water solutions of the copolymer acid anhydride are added to slurries of pulp fibers which have been first treated with PVP. Cross linking of the PVP is initiated by the PVM/MA and is subsequently completed by the heating of the finished product.

The sequence of steps used in the process of the present invention, especially with regard to the addition of PVM/MA, is very important. The PVP is preferably added first to the beaten pulp, either in its pure form or in the form of an aqueous solution. The PVP may also be added together with the modifying resin, although the results obtained thereby will be inferior to those obtained when the PVP is added first by itself. The acidic insolubilizing agent such as PVM/MA must be added subsequent to the treatment of the pulp by the PVP, since if added prior to or together with the PVP, it could precipitate the PVP before the PVP has the opportunity to become attached to the pulp fibers. The acidic insolubilizing agent is added as an aqueous solution. Where aqueous dispersions of a modifying agent such as "A" stage phenolic resins, having alcohol and water as volatile constituents, are used, the PVM/MA may be incorporated directly into the resin dispersion, and subsequently added to the PVP conditioned fibrous slurry. It may also follow the resin treatment, although this is not the preferred sequence. When fillers such as fibers or particles are to be added to the pulp, it has been found effective to treat the fillers with PVP followed by treatment with PVM/MA, all in aqueous solution. The entire mixture is then added to the beater and incorporated with the pulp by mixing.

It has been observed that PVM/MA contributes greatly to insolubilizing, as by cross-linking, the PVP-treated homogeneous pulp-resin complex, particularly where a thermosetting phenolic resin is used, as in the production of post-forming or electrical board stock. As a result, less resin solids will be required while still obtaining comparable physical properties in the finished products.

As an alternative to PVM/MA itself, a modified form thereof may be used for the same purpose, comprising the half-amide of PVM/MA. This form is available commercially in two different grades, "Type 10," a one percent solution having a viscosity of 100–200 centipoises at 25° C., and "Type 30," a solution having a viscosity of 2000–20,000 centipoises. The "Type 10" material having the lower viscosity is preferred. The chemical structure of the half-amide form is as follows:



In the present process, the fiber treating or coupling agents and the modifying materials, comprising resins, are added to the pulp slurry from aqueous systems. Consequently, they must be water-dispersible. Since the coupling agents themselves are infinitely soluble in water, they are introduced in the form of an aqueous solution. Where the modifying materials are themselves dispersible in water, as in the case of water-dispersible phenolic resins the dispersion may be added to the pulp slurry. Where they are not directly water-dispersible, they must be first conditioned, such as by forming into an aqueous emulsion, suspension or colloidal solution, or other suitable form.

In carrying out the present process, the pulp is first beaten to the desired freeness according to prior art methods and standards. During the beating operation, the rolling, shearing and cutting action to which the pulp is subjected, exposes large surface areas of the fibers, and produces many fibrillae to which the coupling agents subsequently become attached.

After the pulp has been sufficiently beaten, and the desired pulp freeness has been attained, the beater roll is raised and the beater itself allowed to circulate. PVP in the desired amount is then added to the circulating pulp. To insure good circulation, the point of addition should preferably be before the raised beater roll. The PVP reacts immediately with the beaten cellulose, opening up the fibers, and, by its wetting action, exposing a larger surface area of the fibers by separating them from each other. It is believed that the PVP becomes adsorbed on the surfaces of the fibrillae in the form of a molecular layer. As a result of the reaction with the PVP, the beaten pulp takes on a slimaceous appearance.

The time required for reacting the beaten pulp with the PVP depends upon the fiber consistency and the degree of circulation of the slurry maintained during treatment. Where a pulp consistency of not greater than three percent is used, a reaction time of from 15 to 30 minutes is generally sufficient. After the reaction is complete, an aqueous dispersion, suspension or emulsion of the modifying material, such as a phenolic resin, or thermoplastic resin, or latex, is added and circulation continued until the modifying material has been substantially removed from the water by the activated pulp.

Since the PVP is infinitely soluble in water, some means must be provided for cross-linking or curing it, so that when the finished paper product is subjected to water, the PVP will not be removed thereby. Where the modifying resin used is a thermosetting resin such a phenolic resin, it may be added directly after the reaction of the PVP with the pulp. When the resin-modified paper is subsequently heated, the thermosetting resin and the PVP-treated pulp become cross-linked whereby the phenolic resin becomes infusible and insoluble with the application of heat. However, where a thermoplastic resin constitutes the modifying agent, the PVP-containing pulp is advantageously treated with an acidic insolubilizing agent. Polymeric anhydride such as PVM/MA or its half-amide, as described above, is the preferred material. Either of these materials may be added directly as aqueous solutions to the PVP-treated pulp, where the reaction is instantaneous. Amounts of PVM/MA which have proven effective are: 1 part PVM/MA to 3 or 4 parts PVP solids. Other acidic materials such as polyacrylic acid may be used as cross-linking agents. Even acids such as acetic acid, sulfuric acid and formic acid have some insolubilizing effect, although they are considerably inferior to PVM/MA.

Since the acidic insolubilizing agent such as PVM/MA or polyacrylic acid is utilized primarily for its function

of insolubilizing the PVP, the amount used will be dependent upon the amount of PVP used. In general, an amount equal to about 20% or 25% of the weight of PVP is satisfactory. An amount equal to or even greater than the weight of PVP may be used, but generally such increase will not be attended by proportionally increased benefits. Amounts less than 20% may be used, particularly when used in conjunction with a thermosetting resin. In fact, as pointed out above, satisfactory results may be obtained when using PVP with a thermosetting resin such as a phenolic, even in the absence of the acidic insolubilizing agent.

The amount of PVP which need be used will vary according to the amount of modifying materials to be added and the type of product to be fabricated. For example, it has been found that about 0.05% of PVP solids based on bone-dry fiber solids, will sufficiently condition pulp to allow small quantities of resin to be thoroughly and completely incorporated. It has additionally been found that an amount of about 0.25% of PVP solids, based on bone-dry fiber solids, is sufficient to incorporate 100 parts of a resin with 100 parts of cellulose fibers. When larger quantities of PVP are utilized, the thickness of the layer thereof on the cellulose fibrillae increases, and the pulp exhibits a greater freeness. At 5% PVP solids addition, based on bone-dry fiber solids, it has been found that the thickness of the layer on the cellulose is of such magnitude that the water drains rapidly upon the deposition of this treated furnish in the couching box. Although amounts greater than 5% may be used, benefits from such increased addition fall off sharply.

Additions of such materials as pigments or insert filler materials should be made to the beaten and reacted pulp at suitable points along the wet-end of the paper making process. Such suitable addition points are at the beater, beater chest, machine chest, or other similar points in advance of the machine headbox. This results in thorough and uniform incorporation. These additive materials may be added in their normal state, or in the form of a water slurry. Prior to their incorporation into the slurry, they may be treated with PVP alone, or with PVP followed by treatment with PVM/MA. Additionally, resins or related materials such as plasticizers and barrier-inducing materials may be incorporated together with the pigment. Regardless of the treatment to which the filler materials are subjected, they should preferably be added to the pulp in the form of a slurry, since this accomplishes the wetting of the solid particles prior to the addition, and aids in the subsequent reation by which the particles are attached to the cellulose fibers. Among the filler materials which may be used are barium sulfate, calcium carbonate, clay, diatomaceous silica, talc, titanium pigments, and zinc sulfide. Various dye stuffs and opacifying pigments, both natural and synthetic, serving as colorants may also be added by the same techniques. They are preferably treated with PVP and combined with any other solids constituting the chemical addition. Upon reaction of the fillers and the other additives with the treated pulp, a complex is formed, and the water becomes clear.

The resinous materials which are suitable for use in the present invention are those which can be readily dispersed in water by one of several means. Where they are not dispersible, many resins may be conditioned by techniques well known to the art, such as by the addition of wetting agents, dispersing agents, or emulsifying agents. Most of the resins commonly used for modification and reinforcement in paper making can be made compatible by means of one of the methods discussed.

The addition of the resin should be made after the pulp has been sufficiently beaten, and after it has been treated with PVP, or with PVP followed by treatment with PVM/MA. The reason for this is that fibrillation of the pulp fibers is promoted by the beating processes. The subsequent treatment of the fibers with PVP, or with PVP and PVM/MA makes available a large charged surface area for adsorbing a large quantity of the resin. Where pigments or inert fillers are to be used in the system they may be added and reacted thoroughly with the treated pulp before the addition of resin takes place. The addition of the resin may then be made. The resin, in the form of a water-dispersion such as a solution, suspension or an emulsion, is added at a low solids content, about 2% to 5% of total solids. High solid resin-varnishes, such as are used in the production of electrical board or post-forming board stock, may not tolerate dilution to this extent. Where this is true, the resin viscosity may be reduced with water to the point just short of the production of a "cloudy condition." The diluted resin is subsequently added in small increments, rather than in the form of a steady stream.

A large variety of resinous materials may be employed, the choice being dictated by the characteristic properties desired in the end product. For example, thermoplastic, elastomeric latex resins may be used for flexibility, while acrylic resins may be used for barrier properties and grease-proofness. Thermosetting resins such as phenolics may be used for rigidity and for electrical properties.

Upon the first addition of the resin, a reaction takes place resulting in an immediate combining or complexing of the PVP-treated pulp with the resin. As further additions are made, a noticeable "slowing down" of the forward movement of the mass in the beater is effected. When large amounts are added, the movement of the pulp stock tends to be reduced considerably. In some instances, when large resin additions are made, the material level of the beater or chest may drop, and frequently requires the addition of water to restore adequate circulation. Mixing should be continued for about 15 to 30 minutes. The stock may, if desired, be water-diluted after about fifteen minutes. The concentrated, beaten, chemically-treated pulp may subsequently be subjected to any suitable paper making operation.

Among the synthetic fibers which may be used as modifying materials are: polyacrylic fibers (Orlon), polyester fibers (Dacron), or polyamide fibers (nylon). The fibers add strength to the final product and may be used to produce dimensionally stable papers, paper boards, pulp-moldings, and steretotype mats. Where polyester fibers such as Dacron are used, they contribute both excellent dimensional stability and dielectric properties to the final product. Because of the hydrophobic nature of most synthetic fibers, it has been found desirable to soak them for a period of about sixty minutes prior to their incorporation into the treated pulp. Soaking may be accomplished by placing the fiber in a water solution of PVP and subsequently PVM/MA or its half-amide. One of several practical techniques may be employed. For example, half of the PVP required may be added to the pulp, and the remaining portion used in the form of a water solution to soak the synthetic fibers. This may be followed by treatment with a solution of PVM/MA or PVM/MA half-amide to insolubilize the PVP. It has also been found that the synthetic fibers may be added by themselves to the beaten, but undiluted and unreacted, pulp in the cycle beater. Subsequently the combined pulp and synthetic fibers are reacted by the addition of a suitable amount of PVP. A longer time-reaction should be allowed for the treatment of the combined fiber slurries.

In addition to synthetic fibers, inorganic fibers such as glass fibers, add strength and dimensional stability as modifiers of the paper making pulp systems. The handling procedure is precisely the same as that previously described. The glass fibers should preferably have a length of about ¼ in. and a fiber diameter of 6 to 9 microns.

Other inorganic fibers, such as asbestos and ceramic fibers, or metallic flakes and powders may also be incorporated as modifiers for the purpose of strengthening the paper product, or for obtaining other properties such as heat or electrical conduction or insulation. Asbestos or ceramic fibers may be prepared by immersing in a PVP

solution for a period of about 60 minutes prior to incorporation with cellulose fibers. They are then added to the hydrated pulp and blended prior to the addition of the resin.

As a means of incorporation of inorganic flake material such as aluminum, dry PVP may be first mixed with the dry aluminum powder or flakes and then slurried with water. Subsequently, the slurry is incorporated into the cellulose stock which has been first treated with PVP. A preferred method, however, is to wet the metallic flakes first with water and PVP solution and subsequently treat the flakes with PVM/MA in order to insolubilize the PVP before it is incorporated into the beater. If desired, the resin component may be combined with the treated aluminum powder and incorporated together therewith into the moving treated pulp stock in the beater. By the present method, very large amounts of aluminum powder may be incorporated into paper stock. No difficulty has been experienced in incorporating equal parts of pulp, aluminum powder and resin. The product so produced has excellent hiding power, and has insulating properties approaching those which may be obtained by the use of aluminum foil. The pulp-aluminum-resin sheet may be calendered to increase its brilliance.

By the substitution of copper powder for the aluminum in the above process, paper board may also be fabricated possessing good heat properties.

The formulation according to the present invention will depend to a large extent upon the properties desired in the end product. For example, long-fibered pulps are effectively used in producing post-forming board and electrical board, whereas shorter-fibered pulps are used for fine papers. Synthetic fibers or inorganic fibers may be used to modify long-fibered stock in order to produce dimensionally stable papers and stereotype mats. For the production of packaging and barrier papers, it has been found desirable to incorporate thermoplastic resins into the pulp. These may be used alone or may be modified with thermosetting resins, or plasticizers to effect such properties as heat sealing, waterproofness, grease-proofness, low moisture-vapor-transmission, and others. Thermosetting resins are generally used to produce post-forming boards which may be subsequently cured to the infusible-insoluble stage, and for the production of electrical boards. Particular chemicals may also be employed as additives where particular properties are desired in the end product.

Among the paper making pulps which may be used in the present invention are the following but not limited thereto: alpha cellulose, cotton linters, rag, recovered broke, semi-chemical, sulfate, sulfite, soda, or mechanical. Any other papermaking pulp may also be employed.

The resins used as additive materials may be modified by the addition of plasticizers of the conventional type which are compatible with the particular resin used, and which are capable of modifying the resins in the desired manner, as for example phthalates, adipates, sebacates, dibenzoates, stearates, and polymeric materials. Other materials such as water soluble glycerides and glycols may also be used.

Among the pigments and inerts which may be added for particular properties are titanium dioxide, various sulfates, clays, zinc sulfide, carbonates, silicates, dyestuffs, talc, and opacifying pigments, both natural and synthetic.

For barrier type products various waxes may be incorporated, such as paraffin, microcrystalline wax, polyethylene, and other natural or synthetic waxes.

A large variety of various resins may be used as modifying agents according to the present invention. As previously stated, in order to incorporate the resins it is necessary that they be dispersible in water, since the paper making process is primarily a water process. Thermoplastics such as various vinyl derivatives, ethylenic resins, rosin and related compounds, natural resins, chlorinated diphenols, cellulose esters and ethers, natural and synthetic rubbers, phenolic resins in the novalac stage, and many others may be advantageously utilized. Where finished products are desired which may be cured to the insoluble, infusible state, thermosetting resins such as phenolics, ureas, melamines, alkyds, polyesters, epoxies, silicones, and many others may be used. Water soluble materials such as proteins, starches carboxymethyl cellulose, glues, resins, caseins, etc., may also be employed.

For particular functional properties, specialized chemicals may be incorporated among which are mold-resistant chemicals, bacteria-resistant chemicals, insect-resistant chemicals, rodent-resistant chemicals, or flame-resistant chemicals.

The pH of the solution is not critical in regard to the effectiveness of the process for conditioning the paper pulp with PVP and with PVM/MA. Satisfactory products may be prepared within a pH range of from about 4.0 to about 8.5.

The amount of modifying agent that may be incorporated is not critical, and will generally depend upon the properties desired in the finished product. By using less than five percent PVP to condition the pulp, it is possible to incorporate a resin such as a phenolic in an amount equal to the weight of the dry pulp.

Amounts of PVP in the range of 0.05% to 5.0%, based on dry weight of pulp, have been found effective. Amounts greater than 5% do not provide a substantial improvement in relation to the amount.

A large number of various types of products may be formed by the processes included within the scope of the present invention. These products may be classified in three main groups: products comprised of cellulose fibers modified by resin, products comprised of cellulose fibers modified by the addition of a resin together with other fibers, and products comprised of cellulose fibers modified by the addition of a resin together with various filler materials other than fibers.

Among the important products of the first group are: post-forming fibrous board stock, electrical board, wet strength papers, barrier papers, battery separators, and laminated structures. Post-forming board may be defined as resin-treated fibrous board stock which has been partially cured, and which may be subsequently heated and molded under heat and pressure to produce a cured product of any desired form. It has been current practice to fabricate such post-forming boards by impregnating or saturating finished paper stock with suitable resins such as liquid phenolic varnishes. After impregnation the excess is generally squeezed free, and the product partially dried and subsequently cured. Other methods have been used, such as sprinkling the paper stock with a dried phenolic resin, forming a laminated structure comprised of several layers of stock and subsequently laminating the structure by heat and pressure. The products of the prior art have been deficient in many respects. Impregnation of the finished stock has resulted in uneven distribution of the resin within the fibrous structure of the board. Moreover, the resin has tended to deposit on the surface and within the superficial interstices, resulting in the production of both "spotty" and "resin-rich" areas.

Post-forming boards may be produced according to the present invention by treating beaten pulp first with PVP, or with PVP followed by treatment with PVM/MA, and finally by the incoporation of a suitable resin while the pulp is still in the slurry stage. Among the resins which may be used are water-dispersible phenol-formaldehyde resins, polyester resins, or epoxy resins. Thermosetting or heat-reactive resins are preferred as they may be molded and cured subsequently to the formation of the board by heating to temperatures in excess of 300° F., under molding pressure.

Current methods used in the art for producing electrical board generally comprise dipping finished paper stock into a saturating tank containing electrical grade phenolic resin varnish, and removing the excess resin by feeding the

saturated paper stock between a pair of squeeze rolls. The impregnated paper then is dried in a suitable drier, cut to a specific size, and laminated under heat and pressure to the desired thickness. Since the cellulose, carrying a negative electrical charge, is repellant to the phenolic varnish, and since the varnish as normally used has a high solids content, adequate penetration of the cellulose is not accomplished, but rather the varnish remains substantially on the surface of the paper stock. Consequently, in order to obtain the desired properties, it is necessary to use a large amount of varnish. Opposed to this, electrical board made by the method of the present invention accomplishes thorough complexing of the individual fibers of the board stock with the resin, and, as a result, the same or better properties can be obtained even though much smaller amounts of varnish are used. Various resins such as phenolformaldehyde, urea-formaldehyde, melamine-formaldehyde, silicones, polyesters, and epoxy resins may be used. Moreover, the less expensive unbleached kraft pulp may be used in the present method while still attaining good electrical properties in the finished product.

A preferred resin for the production of electrical board is a phenol-formaldehyde resole, or "A" stage resin, that is, one which is not yet advanced to the intermediate condensation stage. The formed material is subjected to temperatures of below 250° F. to drive off the water and is then ready for further processing. In order to increase the product strength, various modifying fibers such as acrylic, polyester, acrylonitrile or polyamide may be added to the slurry in the beater treating stage. The formed board stock is subsequently predried to extract any remaining moisture, punched, copper surfaced, pressed cold to level the interstices, printed, etched, and heated under pressure to cure the resin to the infusible and insoluble state.

High wet strength papers may be prepared by beating the pulp stock to the desired freeness, treating it with PVP or PVP followed by PVM/MA, adding the desired resin, and then forming the paper in the normal manner. The paper is subsequently heated to remove moisture and to insolubilize the PVP more completely. Various resins such as acrylics, various elastomers, vinyl polymers and copolymers, urea or melamine thermosetting resins, or various combinations of resins may be used.

Barrier papers may be formed by adding nitrocellulose or ethylcellulose lacquers in the form of dispersions, suspensions, or emulsions to a slurry of pulp which has been pretreated with PVP, or PVP followed by PVM/MA. Prior to treatment with the coupling agent, the pulp is beaten to the desired standard freeness. Among the commercial products which may be formed in this manner are bottle cap liners, fine papers, fire retardant papers, flexible papers, fungicide-proof papers, grease-proof papers, milk containers, hot drink cups, multiwall bags, and many others.

In current practice, cellulose battery separators are prepared by incorporating various resins such as phenolic resins into bibulous cellulosic fiber sheets by the saturation or impregnation techniques. As a result, the product generlly suffers from the same limitations discussed above with respect to other similar products. The present process avoids these limitations by incorporating the resin or other additive material with the cellulose in its discrete fibrous state in the beater, and, as a result, accomplishes an extremely uniform coating about each fiber. Moreover, a final product exhibiting greater desired porosity may be obtained by the present method than by the prior art methods.

Polyester and epoxy laminates may also be prepared by the present invention with minor modifications. In their available industrial form, polyester and epoxy resins cannot be added to the aqueous slurry in the beater since they are not water-dispersible and will not directly combine with the pulp. This condition is overcome by the addition of wetting agents or emulsifiers to the base polyester or epoxy resin, together with the necessary catalyst, and by the subsequent addition of increments of water under moderate to high speed agitation. In their altered form, these resins may be incorporated into the slurry in the beater in accordance with the methods of the present invention. Prior to lamination, the retained moisture of the formed sheets, generally in amounts of from about 5% to 10%, is removed by heating at about 250° F. A plurality of boards is then placed in a press and bonded and cured by the application of suitable heat and pressure.

A second group of products which may be prepared by the present invention are those in which various synthetic fibers are incorporated with the cellulose fibers, in addition to the modifying resin. One of the most important products in this group is dimensionally stable paper, such as map and chart paper, and stereotype mat stock. In preparing these products, the cellulose pulp fibers are treated in the normal manner with successive additions of PVP and PVM/MA and given about a 30-minute mixing period to assure adequate blending. The desired resin is then added to the slurry of treated pulp. Any desirable filler such as inert pigments may be added by previously treating the filler with PVP and PVM/MA, and then adding it to the pulp slurry. The filler may also be mixed together with the required amount of the resin described above and the resulting slurry incorporated as a steady stream into the beater. The beater is then given a 30-minute mixing period to insure that the materials will be adequately incorporated with the pulp. Subsequently, glass fibers, such as those having a diameter of from 6 to 9 microns and a length of about ¼ inch, and which have been previously soaked for about 60 minutes in PVP and PVM/MA, are added. The pulp which has been treated as described is then formed on wet machines to produce commercial stereotype mat stock, or on small screens to form hand sheets, in the usual manner, and dried. The mats or sheets may then be coated and properly conditioned for use in the stereotype process, where the additive resin and fibers will insure the dimensional stability of the mats during use.

Papers which are suitable for use in making dimensionally stable maps and charts may be produced in a manner similar to that described above by incorporating therein various resins, either thermoplastic, or mixtures containing small amounts of thermosetting resins together with thermoplastic resins, and with polyester fibers such as Dacron, or with glass fibers. The processed pulp is then formed on standard paper-making machines and subsequently heat-treated.

A third group of modified paper products which may be made according to the present invention are those in which various fillers other than fibers are incorporated into the pulp, and the pulp subsequently formed into paper or board products. One such product is formed by the incorporation of aluminum powder, preferably in the form of flakes, into the pre-treated pulp slurry in the beater stage. Additives in amounts from about 0.5% to 100%, based on dry pulp weight, may thus be incorporated. In carrying out the process, the pulp is first beaten and then treated with PVP and PVM/MA as described above. The aluminum flakes are then separately treated with PVP or with PVP followed by PVM/MA, the amounts of PVP being from about 0.05% to 0.50% based on aluminum powder solids. When the treated aluminum powder is then added to the beater containing pre-treated pulp, the aluminum powder becomes attached to the pulp fibers, leaving the water clear and free of all particles. The paper or board is then formed from the stock, dried and eventually heat-treated to cure the resinous materials. The final product is non-leafing, has good hiding power, and has heat-insulation values approaching those obtained from aluminum foil. The finished sheets may be further treated by calendering, and

forming into rigid or semi-rigid boards, which may serve as insulating building board, gasket material, or as dimensionally stable stereotype mat stock.

Other additive fillers which may be used together with a resin in the present invention are cork, saw dust, lignin and other related products. These materials are generally light in weight and not easily wetted by water, and therefore difficult to incorporate with the hydrated pulp in prior art paper making processes. It has been found, however, that when they are first treated with PVP and PVM/MA according to the present invention the additive materials are more easily wetted and may be readily incorporated with the treated pulp.

Gasket material may be prepared by incorporating the inorganic fibers, resin binders, or other additives such as cork or asbestos fibers into treated pulp prepared as described above. The additive materials should be treated with PVP or with PVP followed by PVM/MA prior to their incorporation.

Simulated leather paper or board may be prepared by incorporating leather shavings with the cellulose pulp. The shavings or strings should preferably be soaked in PVP and then in PVM/MA prior to incorporation with the pulp. Subsequent to the incorporation of the leather, resins such as acrylonitrile latex, butyl rubber latex, vinyl polymer or copolymer emulsion, thermosetting resins, or modifications of any of these, may be added.

Example 1

One thousand grams of unbleached kraft pulp were charged into a beater containing 12 gallons of water. Beating was continued until a Canadian specific freeness of 400 was obtained. The beater roll was raised and the beater continued in circulation. A solution containing 2.5 grams PVP in water was added to the beater slurry. The PVP is preferably added as a 2% to 5% aqueous solution for ease in handling, although it may be directly added. Circulation in the beater was continued for about 15 minutes until the PVP had been well incorporated. At this point an aqueous dispersion containing 500 grams of a water-dispersible phenolic resin was added to the circulating mixture in the beater. Additional circulation of from 15 to 30 minutes was allowed for the reaction to be completed. From the resulting product, hand sheets were formed on a screen in the usual manner. The resulting product after drying exhibited excellent properties for use as either electrical board or post-forming board.

Example 2

Electrical board stock was prepared as follows. One thousand grams of cotton linters were placed in a beater containing 12 gallons of water. Beating was initiated and continued until a Canadian specific freeness of 307 had been obtained. The beater roll was then raised and the beater continued in circulation. To the circulating mixture, an aqueous solution containing 2.5 grams of PVP was then added. Circulation was continued for about 15 minutes, at the end of which time 600 grams of a water-dispersible phenolic resin in aqueous dispersion were added. This was followed by an addition of 118 grams of nylon fibers. Circulation of the beater was continued for about an additional 30 minutes to complete the reaction. Hand sheets were then formed on a screen and dried. The resulting product was then cured and exhibited properties rendering it suitable for use as electrical board.

As a substitute for the pulps used in the examples above, high alpha cellulose, unbleached rag and bleached kraft may be advantageously used.

Although the use of PVP alone as a coupling agent to react the pulp with resins and other additives, as described in Examples 1 and 2, has been found entirely satisfactory, superior results may be obtained in many instances by treating the pulp with an acid insolubilizing agent such as PVM/MA immediately subsequent to the PVP treatment, and prior to the addition of the resin or additive material. Such procedures are illustrated in the following examples.

Example 3

Into a beater containing 12 gallons of water were added 1000 grams of unbleached kraft. Beating was continued until the desired freeness had been obtained, at the end of which time the beater roll was raised and the moving stock was treated with an aqueous solution containing 2.5 grams of PVP solids. The beater was allowed to circulate for an additional fifteen minutes. At the end of this period 0.5 gram PVM/MA in the form of a water solution was added to the PVP-treated pulp. Circulation was continued for an additional 15 to 30 minutes. An aqueous dispersion containing five hundred grams of a water-dispersible phenolic resin was then added to the beater mixture, and the beater was allowed to circulate for still an additional 15 to 30 minute period. At the end of this time, hand sheets were formed on a screen and subsequently dried. The dried hand sheets were formed into electrical board by curing the resin-containing pulp product to the infusible insoluble state by heat and pressure. The end-product possessed excellent hardness, rigidity, dimensional stability, and high compression strength and modulus of elasticity at elevated temperatures.

Example 4

Three thousand pounds of mixed pulp were introduced into a commercial size beater. Beating was continued until a Williams freeness of 305 had been attained. The finished material from the beater was then dropped into a beater chest and sufficient water added to effect a 3% consistency. Thereafter, PVP as an aqueous solution was added to the circulating chest in an amount sufficient to give 0.250% PVP solids by weight based on the pulp solids. The chest was circulated for one hour. PVM/MA solids dissolved in aqueous solution, and in the amount equal to 20% based on PVP solids, were then incorporated into the PVP-treated pulp. Circulation was continued for one hour. A mixture of clay and hydrous oxides in equal amounts was separately slurried with water containing 0.125% PVP solids, based on total inert solids of 700 pounds. This was added to the chest and circulation was continued for one hour. Twenty percent of PVM/MA solids in aqueous solution and based on PVP solids were then incorporated and reacted with the PVP-treated inert solids.

A reactive water dispersible phenol-formaldehyde resin and an emulsifiable type of polyester resin were then separately water-diluted to non-volatile solids of 3% and incorporated with the moving mass in the circulating chest. Circulation was continued for 1½ hours to insure thorough incorporation of all added solids. Thereafter the treated pulp was reduced to 1½% consistency and pumped to the wet machine-head box where the consistency was reduced to 0.1%. The material was then formed on a standard roll used in the art for forming stereotype mat stock, and, when dried resulted in mat stock having excellent dimensional stability.

Example 5

A novel aluminum flake-containing board stock was prepared by first beating 1000 grams paper pulp for 90 minutes to a Canadian standard freeness of 187. The roll was then raised and 0.94% PVP solids in aqueous solution were added to the slurry. After circulation had continued for 15 minutes, 0.185% PVM/MA solids was added to the mixture and circulation continued for an additional 15 minutes. At the end of this period, 250 grams aluminum flake powder which had been previously treated with 0.63% PVP solids and 0.13% PVM/MA solids, each as aqueous solutions, were added in aqueous slurry form to the beater and an additional 10 minutes of circulation allowed. An aqueous dispersion of 250

grams phenol-formaldehyde resin solids was then added and circulated for still another 15 minutes. At the end of this period the slurry was couched off on a paper-making screen leaving clear white water, and dried. The resulting product was then heated to set the resin and resulted in aluminum-containing board which was non-leafing, had good hiding power, and good heat insulation values.

The following examples contain formulations for the preparation of various commercial products. Although detailed methods are not given with each formulation, the methods described above generally, and described in Examples 1 to 5 more specifically, may be used. The pulp may be conditioned as described above, particularly in Examples 1, 2 and 3. All resinous materials should be dispersed in an aqueous medium, either as a suspension, emulsion, or any other suitable dispersed form. Other additives in addition to resins should preferably be soaked in an aqueous solution of PVP, or PVP followed by PVM/MA prior to their incorporation into the pulp slurry. Each material addition should be followed by sufficient circulation to insure proper distribution.

The following example contains a formulation for the production of post-forming board stock.

Example 6

	Parts
Pulp	100
PVP	0.25
PVM/MA	0.05
Water dispersible phenol-formaldehyde resin	11

The examples immediately following present formulations for the production of electrical board stock.

Example 7

	Parts
Pulp	100
PVP	1.00
PVM/MA	0.20
Water-dispersible phenol-formaldehyde resin	100

Example 8

Pulp (cotton linters)	100
PVP	0.25
PVM/MA	0.05
Water-dispersible phenol-formaldehyde resin	60
Glass fibers	5

Example 9

Pulp	100
PVP	0.375
PVM/MA	0.019
Water-dispersible phenol-formaldehyde resin	50

Example 10

Pulp	100
PVP	0.25
PVM/MA	0.05
Water-dispersible phenol-formaldehyde resin	60
Orlon fibers	10

Example 11

Pulp	100
PVP	5.00
PVM/MA	1.00
Water-dispersible phenol-formaldehyde resin	100

The following examples present formulations for the preparation of barrier paper stock.

Example 12

	Parts
Pulp	100
PVP	0.25
PVM/MA	0.80
Butyl rubber latex	11
Acrylate polymer	4

Example 13

Pulp	100
PVP	0.5
PVM/MA	0.45
(Buna N) Rubber latex	10

The following examples present formulations for the preparation of dimensionally stable stereotype mat stock.

Example 14

	Parts
Pulp	100
PVP	0.50
PVM/MA	0.10
Clay	11.5
Hydrous oxide of silicon	11.5
Water-dispersible phenol-formaldehyde resin	5

Example 15

Pulp	100
PVP	0.375
PVM/MA	0.10
Water-dispersible phenol-formaldehyde resin	5
Clay	11.5
Hydrous oxide of silicon	11.5
Glass fibers	7.5

The following example lists the formulation for the preparation of gasket material stock.

Example 16

	Parts
Pulp	100
PVP	0.375
PVM/MA	0.075
Water-dispersible phenol-formaldehyde resin	27.5
Butyl rubber latex	10
Asbestos fibers	50

The following examples illustrate the formulation for the preparation of metal powder-containing paper or board stock.

Example 17

	Parts
Pulp	100
PVP	0.375
PVM/MA	0.10
Water-dispersible phenol-formaldehyde resin	100
Aluminum flake powder	100

Example 18

Pulp	100
PVP	0.25
PVM/MA	0.055
Buna N latex	15
Aluminum flake powder	10

Example 19

A pilot plant run was made utilizing unbleached kraft pulp and heat reactive phenol-formaldehyde resin in the production of post-forming board. 200 pounds air dried pulp were charged to the semi-production beater and beaten to a Canadian freeness of 520. The beaten pulp was finish-treated in the beater. One-half pound of PVP-solids in aqueous solution was reacted with the pulp, followed by 1/10 pound PVM/MA solids in aqueous solution. Thereafter 20 pounds phenol-formaldehyde resin as water-dispersible solids were introduced and reacted with the PVP-PVM/MA treated pulp. Complexing of the solids occurred rapidly. The beaten mass was then diluted to 1½% consistency and pumped to the wet machine where consistency was reduced to 0.1%.

The prepared board stock was taken off the machine cylinder and placed on the drying drum for smoothing and expulsion of moisture. The board stock was dried down to about 5% contained moisture. Sheets were cut to fit the size of the die mold. Sheets were first dried at 270° F. to eliminate all moisture and to preclude any

blistering. Thereafter sheets were formed at 325° F. under 1000 p.s.i. for 30 minutes. This resulted in the production of post-formed products of excellent properties.

Although the present invention has been illustrated in only relatively few embodiments, it is to be understood that many variations may be practiced by those skilled in the art without departing from the spirit and scope of the invention as defined by the appended claims.

Invention is claimed as follows:

1. A process for depositing a water-dispersible resin on beaten cellulose pulp fibers comprising first dispersing polyvinylpyrrolidone into an aqueous slurry of said fibers, and subsequently dispersing said resin into said slurry, the polyvinylpyrrolidone being added in an amount of at least about 0.05% by weight based on the dry weight of said pulp fibers.

2. A process for depositing a resin coating on beaten cellulose pulp fibers comprising first adding polyvinylpyrrolidone to an aqueous slurry of said fibers and mixing said slurry to deposit said polyvinylpyrrolidone on said fibers, and then adding an aqueous dispersion of said resin to said slurry and mixing said slurry until said resin is deposited on said fibers, the polyvinylpyrrolidone being added in an amount of at least about 0.05% by weight based on the dry weight of said pulp fibers.

3. A process for depositing a water-dispersible resin on beaten cellulose fibers comprising the steps of dispersing polyvinylpyrrolidone into an aqueous slurry of said fibers, then dispersing a minor proportion of a water-soluble acidic insolubilizing agent into said slurry in an amount sufficient to insolubilize said polyvinylpyrrolidone, and subsequently dispersing said resin into said slurry, the polyvinylpyrrolidone being added in an amount of at least about 0.05% by weight based on the dry weight of said pulp fibers.

4. A process for depositing a water-dispersible resin on beaten cellulose pulp fibers comprising the steps of uniformly dispersing an aqueous solution of polyvinylpyrrolidone into an aqueous slurry of said fibers, then uniformly dispersing an aqueous solution of a polymeric acid anhydride into said slurry in an amount sufficient to insolubilize said polyvinylpyrrolidone, and subsequently uniformly dispersing an aqueous dispersion of said resin into said slurry, the polyvinylpyrrolidone being added in an amount of at least about 0.05% by weight based on the dry weight of said pulp fibers.

5. A process for depositing a water-dispersible resin on beaten cellulose fibers comprising the steps of dispersing polyvinylpyrrolidone into an aqueous slurry of said fibers, next dispersing a water-soluble copolymer of vinylmethylether and maleic anhydride into said slurry in an amount sufficient to insolubilize said polyvinylpyrrolidone, and subsequently dispersing said resin into said slurry, the polyvinylpyrrolidone being added in an amount of at least about 0.05% by weight based on the dry weight of said pulp fibers.

6. A process according to claim 5 wherein said polyvinylpyrrolidone is added in an amount from about 0.05% to about 5% by weight based on the dry weight of said pulp, and said copolymer is added in an amount from about 20% to about 25% based on the dry weight of said polyvinylpyrrolidone.

7. A process for depositing a water-dispersible phenol-formaldehyde resin on beaten cellulose fibers comprising the steps of first dispersing polyvinylpyrrolidone into a slurry of said fibers, next dispersing a copolymer of vinylmethylether and maleic anhydride into said slurry, and finally dispersing said resin into said slurry, the polyvinylpyrrolidone being added in an amount of from about 0.05% to about 5% by weight based on the dry weight of said pulp and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

8. A process for depositing an emulsifiable synthetic resin on beaten cellulose pulp fibers comprising the steps in sequence of dispersing an aqueous solution of polyvinylpyrrolidone into an aqueous slurry of said fibers, dispersing an aqueous solution of a copolymer of vinylmethylether and maleic anhydride into said slurry, and dispersing said resin in emulsion form into said slurry, the polyvinylpyrrolidone being added in an amount of from about 0.5% to about 5.0% by weight based on the dry weight of said pulp fibers and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

9. A process for depositing an elastomer in latex form on beaten cellulose pulp fibers comprising the steps in sequence of dispersing an aqueous solution of polyvinylpyrrolidone into an aqueous slurry of said fibers, dispersing an aqueous solution of a copolymer of vinylmethylether and maleic anhydride into said slurry, and dispersing said latex into said slurry, the polyvinylpyrrolidone being added in an amount of from about 0.5% to about 5.0% by weight based on the dry weight of said pulp fibers and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

10. A process for depositing a water-dispersible resin on beaten cellulose pulp fibers comprising the steps in sequence of uniformly dispersing polyvinylpyrrolidone into an aqueous slurry of said fibers, uniformly dispersing a copolymer of the half-amide of vinylmethylether and maleic anhydride into said solution, and dispersing an aqueous dispersion of said resin into said slurry, the polyvinylpyrrolidone being added in an amount of from about 0.5% to about 5.0% by weight based on the dry weight of said pulp fibers and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

11. A modified paper which may be molded at elevated temperature and pressure, said paper having been prepared by the steps in sequence of dispersing polyvinylpyrrolidone into an aqueous slurry of beaten cellulose pulp fiber, dispersing a copolymer of vinylmethylether and maleic anhydride into said slurry, dispersing a water-dispersible resin into said slurry, and forming said paper from said pulp fibers on a paper making machine, the polyvinylpyrrolidone being added in an amount of from about 0.5% to about 5.0% by weight based on the dry weight of said pulp fibers and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

12. A dimensionally stable stereotype mat prepared by the steps in sequence of dispersing polyvinylpyrrolidone into an aqueous slurry of beaten cellulose pulp fibers, dispersing a copolymer of vinylmethylether and maleic anhydride into said slurry, dispersing a water-dispersible synthetic resin, a water dispersion of inert fillers and a minor proportion of discrete dimensionally stable fibers into said slurry, and forming said mat from said treated pulp on a paper making machine, the polyvinylpyrrolidone being added in an amount of from about 0.5% to about 5.0% by weight based on the dry weight of said pulp fibers and said copolymer being added in an amount sufficient to insolubilize said polyvinylpyrrolidone.

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