

[54] SEQUENTIAL ADDITION OF A CATIONIC DEBONDER, RESIN AND DEPOSITION AID TO A CELLULOSIC FIBROUS SLURRY

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[58] Field of Search 162/169, 182, 183, 168, 162/158; 128/284, 285; 260/85.5 S

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[57] **ABSTRACT**

Cellulosic sheet materials are produced from a slurry comprising cellulosic fibers to which there is added sequentially a cationic surface active agent, a resin selected from the group consisting of acrylic emulsions and anionic styrene-butadiene latexes and a deposition aid for the resin.

18 Claims, No Drawings

SEQUENTIAL ADDITION OF A CATIONIC DEBONDER, RESIN AND DEPOSITION AID TO A CELLULOSIC FIBROUS SLURRY

This is a continuation, of application Ser. No. 108,638 filed Jan. 21, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to improved cellulosic sheet materials and to a method of preparing said materials. More particularly the invention relates to cellulosic sheet materials prepared from a furnish comprising cellulosic fibers; at least one debonder selected from the group consisting of anionic and cationic surface active agents; at least one resin selected from the group consisting of acrylic emulsions and anionic styrene butadiene latexes; and, when the debonder is an anionic surface active agent, a deposition aid for the resin.

2. Description of the Prior Art

The production of sheet materials from cellulosic fibers generally begins with an aqueous slurry of the fibers, said slurry being commonly referred to as a furnish. In the preparation of sheet material the furnish is cast onto a wire surface so that the water is removed and the fibers brought into close contact with one another. While in this close contact, hydrogen bonds are formed between the hydroxyl groups of adjacent fibers resulting in the production of a sheet material, the strength of which is due to this natural fiber-to-fiber bonding.

For certain applications, such as paper towels, tissues, and sanitary napkin and diaper covers it is also necessary that the sheet produced be soft, in the sense that it is sufficiently soft to the touch to be acceptable by the public. It is also essential that these soft products have sufficient strength, both for their production on conventional sheet forming equipment and for their intended use.

Several methods have heretofore been suggested for obtaining a product having the requisite softness. However, these methods, and products produced thereby, have not achieved widespread commercial success due to one, or more, of several inherent disadvantages. Those which require machine modifications cannot be run on existing, high-speed, sheet forming equipment. Others, which require a mechanical treatment of the sheet after it is formed, such as creping, perf-embossing and texturizing, result in a somewhat softer sheet but the increase in softness is accompanied by a significant decrease in tensile strength placing practical limitations on the improvement in softness which can be achieved. Chemical additives have also been employed to achieve softness in cellulosic sheet materials. Those which are applied to the formed sheet generally are difficult to apply, requiring the use of baths or sprays, and do not produce products having the desired combination of softness and strength. Chemicals which can be added to the pulp furnish prior to the sheet forming operation are easier to work with but the products produced therefrom have not heretofore possessed the desired properties of softness and strength. Certain chemical additives, commonly referred to as debonding agents, when added to the furnish interfere with the natural fiber-to-fiber bonding during the sheet forming operation. With these additives it has often been difficult to control the quality of the product produced and, al-

though certain of these additives have imparted some degree of softness to the resulting product, this improvement has been accompanied by a significant decrease in the tensile strength of the product produced.

In much of the prior art, it is recognized that any increase in softness will be accompanied by a significant decrease in tensile strength, and softness is often measured by this decrease in tensile strength.

Other chemicals, such as aqueous-based dispersions of resinous materials, have also been suggested for use in cellulosic sheet materials. These chemicals have been employed primarily to increase the strength of the sheet. However, by increasing the strength of the sheet these additives also resulted in a harsher, or less soft, sheet which could only be avoided by selecting a different additive. And, here also, no significant improvement in softness has resulted.

Besides the above-mentioned problems previously employed additives have often introduced other undesirable properties, such as odor, decreased water-adsorbency, etc., into the final product.

SUMMARY OF THE INVENTION

In accordance with the present invention, cellulosic sheet materials having improved softness and acceptable tensile strength are produced from a furnish comprising cellulosic fibers; at least one debonder selected from the group consisting of anionic and cationic surface active agents; a resin selected from the group consisting of acrylic emulsions and anionic styrene butadiene latexes; and, when the debonder is an anionic surface active agent, a deposition aid for the resin.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In carrying out the present invention an aqueous slurry of cellulosic fibers is prepared according to any well-known method. This aqueous slurry, or furnish, is then treated with chemicals in the beater, stock chest, fan pump, headbox or at any other suitable point ahead of the fourdrinier wire, or sheet forming stage.

The chemical treatment comprises at least one resin and one debonder, as hereinafter defined. However, since the charge on the cellulosic fibers is anionic, and the resins which have been found to be useful in carrying out the present invention can also be anionic or nonionic, it is often necessary to add a third component, or deposition aid, which causes the resin to adhere to the fibers. A separate deposition aid is not necessary when a cationic surface active agent is employed as the debonder and is added to the pulp furnish prior to the addition of the resin. Neither is a deposition aid required with a cationic resin. However, to insure complete deposition of the resin onto the fibers it is especially preferred to add the deposition aid in all cases.

After the chemical treatment, sheets are prepared from the furnish according to any well-known method.

The various chemical additives employed in carrying out the present invention can be defined as follows:

Deposition Aids

The deposition aids which have been found to be useful in carrying out the present invention include those compounds which are known to be useful for depositing a water-insoluble polymer onto cellulosic fibers. These compounds include vinyl imidazoline polymers, such as those disclosed in U.S. Pat. No. 3,527,719 and

in British Pat. No. 1,052,112, and polyquaternary ammonium compounds, such as those described in U.S. Pat. No. 2,765,229. Commercially available compounds which have been found to be particularly useful include Lufax 295, a cationic polyelectrolyte solution polymer that functions as a coupling agent in the beater addition of acrylic emulsions to cellulose and normally available from Rohm and Haas Company, Philadelphia, Pennsylvania; as a tan powder which is a salt complex of a polyamine having a solids content of 100 percent; a pH for a 1 percent aqueous solution of 1.8 and a viscosity for a 10 percent solids solution of 3,300 cps as determined by a Brookfield Viscometer LVT at 25°C, with a No. 4 spindle at 60 r.p.m.; Resin s243, a cationic aqueous solution of a quaternary chloride solution polymer also available from Rohm and Haas; as a clear amber liquid having about 32 percent solids content, a pH of 2.0, a density at 25°C of 9.0 lbs. per gallon and a viscosity of 250 cps as determined by a Brookfield LVF Viscometer at 20°C with a No. 1 spindle at 12 r.p.m. and Quaker 2000, a cationic, high molecular weight, quaternized ammonium imidazoline sulfate available from Quaker Chemical Corporation, Conshohocken, Pennsylvania and having a pH of about 3.4 for a 3.2 percent dilution in water at 77°F; a saybolt viscosity at 100°F of 2500 to 2900 seconds; a kinematic viscosity at 100°F of 530 to 630 centistokes and a pour point of below 0°F. The Quaker 2000 can function as both a coupler and a debonder.

The amount of deposition aid employed can be varied over a wide range depending on the type of furnish employed, the amount of resin to be deposited, and other variables associated with the sheet forming operation. It is especially preferred to employ an amount equal to from about 0.1 percent to about 3.0 percent based on the oven dry weight of the fibers employed. To insure complete deposition of the resin on the fibers it is preferred to add up to 0.5 percent of the deposition aid after the resin has been added. When this procedure is employed the order of addition to the furnish is deposition aid, resin, deposition aid.

Resins

The resins which can be employed in carrying out the present invention include acrylic emulsions and anionic styrene-butadiene latexes. These resins can be used either alone or in combination with other resins such as those which are commonly used to improve the wet strength of cellulosic sheet materials, namely the urea-formaldehyde and melamine formaldehyde type resins. Commercially available resins which have been found to be particularly useful include Rhoplex K3 a nonionic self-crosslinking acrylic emulsion available from Rohm and Haas Company, Philadelphia, Pennsylvania; Rhoplex P339, an anionic self-crosslinking acrylic emulsion, also available from Rohm and Haas Company as a milky white liquid having a 44 percent solids content with a pH of 4.8, a density at 25°C of 8.8 lbs. per gallon, a glass transition temperature of +3°C, a minimum film formation temperature of 0°C and a viscosity at 25°C of 43 cps as determined by a Brookfield Viscometer LVT employing a No. 1 spindle at 60 r.p.m.; Goodrite 2570 × 15, an anionic, carboxylated styrene-butadiene copolymer containing in excess of 70 percent butadiene available from B. F. Goodrich Chemical Company, Cleveland Ohio; and Tylac RB 1118, an anionic, carboxylated styrene-butadiene copolymer containing ap-

proximately 50 percent styrene from Standard Brands Chemical Corporation, Dover, Delaware. The following anionic, self-crosslinking, acrylic emulsions available from Rohm and Haas Company have also been found to be particularly useful — Rhoplex E631, Rhoplex E610, and Rhoplex TR407. Other useful commercially-available resins include Pliolite 610, a styrene-butadiene latex from B. F. Goodrich Chemical Company, and Rhoplex E32 a nonionic, self-crosslinking acrylic emulsion from Rohm and Haas Company. An additional resin, which has been found to be useful in carrying out the present invention, is a cationically dispersed acrylic emulsion comprising about 68 parts ethylacrylate and about 32 parts styrene.

The amount of resin employed can be varied over a wide range depending upon the properties desired in the final product, the amount of resin retained on the fibers, and other variables associated with the sheet forming operation. It is especially preferred to employ an amount of resin equal to from about 3.0 percent to about 15.0 percent of the oven dry weight of the fibers employed.

Debonders

The debonders which can be employed in carrying out the present invention include anionic and cationic surface active agents. Especially preferred are cationic quaternary ammonium compounds including imidazolium compounds such as Quaker 2000 and Velvetol CHR, high molecular weight quaternized imidazolines, available from Quaker Chemical Corporation, Conshohocken, Pennsylvania. Other preferred cationic quaternary ammonium compounds are the alkyl ammonium salts such as dihydrogenated tallow dimethyl ammonium chloride, available from General Mills Inc., Chemical Division, Kankakee, Illinois as Aliquat H226; dialkylamide diethyl ammonium sulfate available from Reichold Chemicals Inc., White Plains, New York as Rycofax 618; and Rycofax 637, an amphoteric quaternary ammonium compound also available from Reichold Chemicals Inc.

Anionic surface active agents which are also preferred for use as debonders in carrying out the present invention include compounds such as sodium tetradecyl sulfate available as Tergitol Anionic 4 from Union Carbide Corporation, New York, New York and the sodium salt of sulfated nonyl phenoxy poly(ethylene oxy) ethanol available as Alipal AB436 from General Aniline and Film Corporation, New York, New York.

The amount of debonder employed can be varied over a wide range depending upon the furnish employed, the properties desired in the final product and other variables associated with the sheet forming operation. It is especially preferred to employ an amount of debonder equal to from about 0.15 percent to about 2.0 percent of the oven dry weight of the fibers employed.

The debonder may be added either before or after the resin or resin-deposition aid combination. When the furnish comprises 100 % wood pulp it is preferred to add the debonder following the deposition of the resin onto the fibers. However, when the furnish comprises wood pulp and synthetic fibers, such as rayon, for example, it is preferred to add the debonder prior

to the addition of the resin or the deposition aid-resin combination.

In order to describe the present invention so that it may be more clearly understood, the following examples are set forth in which all percentages of chemical additives are based on the oven-dry weight of the pulp employed. The physical properties reported herein were obtained using the following test procedures, except as otherwise noted in the examples.

Handsheets were prepared on a standard Noble and Wood handsheet machine.

Basis weight of the sheets was determined by weighing eight sheets measuring 2 ½ inches × 2 ½ inches and converting the result to pounds/ream (2880 square feet).

Tensile strength was determined with a standard Instron Tensile Tester using 1 inch wide test strips, a span of 2 inches and a strain rate of 2 inches per minute.

Fold value and crush value were measured on an apparatus designed to give an indication of the softness of a sheet by measuring the force required to fold the sheet (the fold value) and the force required to crush the folded sheet (the crush value). A decrease in these values is indicative of a softer sheet. The apparatus employed to obtain these measurements comprises an inner set of circular platens and an outer set of annular platens. The platens are arranged so that there is an upper and lower member of each set. The upper circular platen has a diameter of 1.09 inches and a rounded edge having a radius of 0.062 inches. The lower circular platen has a diameter of 1.43 inches and is located directly below the upper circular platen. The upper annular platen has an inside diameter of 2.125 inches and a rounded inner edge also having a radius of 0.062 inches. The lower annular platen is of similar size and is located directly below the upper annular platen. The rounded edges of the two sets of platens are separated by a distance of 0.382 inches. The upper member of each set of platens is attached to means for clamping that set of platens together and the surfaces of all the platens are highly polished.

There is also included, below the space between the two sets of platens a circumferential ring attached to means for moving said ring through said space. The ring has an inner diameter of 1.5 inches, an outer diameter of 1.75 inches and the rounded portion has a radius of 0.062 inches. Above the space is another annular platen having an inside diameter of 1.16 inches and an outside diameter of 2.062 inches. This platen is also highly polished and is attached to means for moving said platen towards the space.

In operation the sheet to be tested is placed between the upper and lower members of the two sets of platens. The inner circular set of platens is clamped to hold the sheet in place and the distance between the upper and lower members of the outer annular set is adjusted to 0.065 inches. The distance the circumferential ring will travel is adjusted to 0.250 inches and a force is applied to said ring causing it to move in an upward direction through that distance folding the sheet as it moves. The maximum force on the ring during this folding operation is recorded in grams and is referred to as the fold value of the sheet.

After the sheet is thus folded the outer annular set of plates is clamped to maintain the sheet in the folded condition. The folded sheet is crushed by, simultaneously, moving the circumferential ring down way

from the sheet and moving the annular platen down onto the sheet for a distance of 0.050 inches. The maximum force on the platen as it moves through this distance is measured in grams and is referred to as the crush value of the sheet.

Sheets produced in accordance with the present invention are characterized by their improved softness which is achieved without a significant decrease in tensile strength and are useful in sanitary products such as tissues, paper towels, and sanitary napkin and diaper covers.

The following examples are set forth primarily for the purpose of illustration, and any specific enumeration of detail contained therein should not be interpreted as a limitation on the concept of this invention.

EXAMPLE I

A wood pulp slurry was prepared comprising 60 % bleached Kraft softwood pulp and 40 percent bleached Kraft hardwood pulp. The slurry was slushed in a British disintegrator at a consistency of 0.5 percent for 15 minutes. Noble and Wood handsheets were prepared from a sample of this furnish. When tested, as described above, these sheets had the following physical properties:

Basis weight	9.8
Fold value	331
Crush value	104
Tensile strength	9.5

A second sample of this furnish was placed in a Hobart Kitchen Aid Mixer Model No. K-45 available from Hobart Manufacturing Company, Philadelphia, Pennsylvania operating at 60 rpm and 1 percent, based on the oven-dry weight of the fibers, of Quaker 2000 a high molecular weight quaternized imidazoline sold by Quaker Chemical Corporation, Conshohocken, Pennsylvania, was added. Noble and Wood handsheets were prepared and tested. These sheets had the following physical properties:

Basis weight	10.3
Fold value	156
Crush value	25
Tensile strength	2.0

To a final sample of this furnish in the Hobart Mixer was added sequentially at 5 minute intervals, 2.5 percent Lufax 295, a cationic deposition aid sold by Rohm and Haas Company, Philadelphia, Pennsylvania, 9.0 percent Rhoplex TR 407 an anionic self crosslinking acrylic emulsion also sold by Rohm and Haas Company, 0.3 percent Lufax 295 and 1 percent Quaker 2000. Noble and Wood handsheets prepared from this furnish had the following physical properties

Basis weight	10.2
Fold value	244
Crush value	63
Tensile strength	7.5

Example II

A wood pulp furnish of beaten bleached Kraft softwood pulp was prepared as in Example I. Noble and Wood handsheets prepared from a sample of this furnish had the following physical properties:

Basis weight	10.1
Fold value	795
Crush value	386
Tensile strength	39.6

To a sample of this pulp, in a Hobart Mixer set at 60 rpm, was added 2.0 percent of Quaker 2000. Handsheets prepared from this furnish had the following physical properties:

Basis weight	10.1
Fold value	237
Crush value	68
Tensile strength	6.0

Another sample of the pulp was treated, in a Hobart Mixer, with the following chemicals added sequentially at 5 minute intervals, 0.075 percent Lufax 295, 5.0 percent Rhoplex P339, an anionic self crosslinking acrylic emulsion sold by Rohm and Haas Company, Philadelphia, Pennsylvania, 0.025 percent Lufax 295 and 2.0 percent Quaker 2000. Handsheets prepared from this furnish had the following physical properties:

Basis weight	10.4
Fold value	336
Crush value	108
Tensile strength	14.7

Example III

A bleached Kraft hardwood pulp furnish was prepared at 1.5 percent consistency. 0.50 percent Quaker 2000 was added and the furnish was stirred for five minutes. At the end of this time the consistency was reduced to 1 percent and the following chemicals were added sequentially at 5 minute intervals:

- 0.14 percent Resin S-243 available from Rohm and Haas Company, Philadelphia, Pennsylvania
- 7.0 percent Rhoplex P339 also available from Rohm and Haas Company, and
- 0.007 percent Resin S243.

After an additional five minutes of mixing, rayon fibers were added so that 15 parts of $\frac{3}{4}$ inch - 5.5 denier rayon, 5 parts of $\frac{1}{2}$ inch - 1.5 denier rayon and 5 parts of $\frac{1}{4}$ inch - 1.5 denier rayon were added for every 75 parts of wood pulp in the furnish.

Noble and Wood handsheets were prepared by the standard method described above except that the fabric was couched off the screens onto standard British handsheet blotters before being pressed and dried. Handsheets prepared in this manner had the following physical properties:

Basis weight	40.6
Fold value	494
Crush value	334
Tensile strength	32.6

By comparison sheets containing only 0.5 percent Quaker 2000 had the following physical properties:

Basis weight	40.5
Fold value	298
Crush value	273
Tensile strength	10.0

and those with no additives had the following physical properties:

5	Basis weight	40.0
	Fold value	575
	Crush value	above 480
	Tensile strength	31.6

In this example, tensile strength was measured with a standard Instron Tensile Tester using a test span of 4 inches rather than the 2 inch test span used in the other examples. In obtaining the fold and crush values the piece of apparatus described above was employed with the following modifications. In operation the distance between the upper and lower members of the outer annular set of platens was set at 0.10 inches rather than 0.065 inches. The distance the circumferential ring travelled in obtaining the fold value was set at 0.075 inches rather than 0.250 inches. The distance the annular platen moved down onto the sheet to obtain the crush value was set at 0.025 inches rather than 0.050 inches.

Example IV A wood pulp furnish at 3 percent consistency was prepared comprising 40 percent bleached Kraft hardwood, 30 percent bleached Kraft softwood and 30 percent bleached sulfite softwood. The furnish was treated, in the beater chest of a pilot plant Fourdrinier paper machine, with the following chemicals which were added sequentially at 5 minute intervals:

- 0.3 percent Lufax 295
- 0.17 percent Nopco DF-160L defoamer available from Nopco Chemical Company, Newark, New Jersey, and
- 10.0 percent Rhoplex P339.

About 0.5 percent Quaker 2000 was added continuously into the return leg of the machine chest stuff box and about 1.0 percent melamine formaldehyde resin was added into the outlet side of the stuff box. The pH of the stock system was maintained at approximately 4 with sulfuric acid.

Sheets were prepared from this furnish at a machine speed of approximately 150 feet/minute and the product was wet-creped. These sheets had the following physical properties:

50	Basis weight	30.0
	Tensile strength (MD)	90
	Tensile strength (CD)	44
	Fold value	292
	Crush value	92

By comparison the same furnish, without any chemical additives, produced sheets with the following physical properties:

60	Basis weight	29.0
	Tensile strength (MD)	84
	Tensile strength (CD)	44
	Fold value	520
	Crush value	158

In this example, the fold and crush values were obtained using the apparatus described above with the following modifications. In operation the distance between the upper and lower members of the outer annular set of platens was set at 0.10 inches rather than 0.065 inches. The distance the circumferential ring

travelled in obtaining the fold value was set at 0.125 inches rather than 0.250 inches. The distance the annular platen moved down onto the sheet to obtain the crush value was set at 0.095 inches rather than 0.050 inches.

Example V

A bleached Kraft softwood pulp furnish was prepared as in Example I and treated, in a Hobart Mixer at 60 rpm, with the following chemicals added sequentially at 5 minute intervals, 0.20 percent Lufax 295, 3.0 percent Rhoplex P339, 0.065 percent Lufax 295 and 0.25 percent Quaker 2000. Noble and Wood handsheets prepared from this furnish had the following physical properties:

Basis weight	9.9
Fold value	242
Crush value	51
Tensile strength	8.6

By comparison handsheets made from the same furnish without the chemical additives had the following physical properties:

Basis weight	10.5
Fold value	451
Crush value	144
Tensile strength	16.9

Example VI

A wood pulp furnish, comprising 60 percent bleached Kraft softwood pulp and 40 percent bleached Kraft hardwood pulp, was prepared as in Example I. Noble and Wood handsheets prepared from this furnish had the following physical properties:

Basis weight	10.3
Tensile strength	12.2
Fold value	400
Crush value	148

A sample of the pulp was treated, in a Hobart Mixer operating at 60 rpm, with 0.15 percent Quaker 2000. Handsheets prepared from this sample had the following physical properties:

Basis weight	10.3
Tensile strength	5.9
Fold value	254
Crush value	83

A second sample of the pulp was treated with the following chemicals added sequentially at 5 minute intervals - 0.225 percent Lufax 295, 15 percent Hycar 2500 X 138, a self crosslinking, anionic, acrylic emulsion available from B. F. Goodrich Chemical Company, Cleveland, Ohio, 0.015 percent Lufax 295 and 0.15 percent Quaker 2000. Handsheets prepared from this sample had the following physical properties:

Basis weight	10.2
Tensile strength	12.3
Fold value	363
Crush value	128

Example VII

A beaten, never-dried, bleached sulfite softwood pulp furnish was prepared, as in Example I, and treated, in a Hobart Mixer operating at 60 rpm, with the following chemicals, added sequentially at 5 minute intervals - 0.2 percent Lufax 295, 5.0 percent Rhoplex K3 of a nonionic self crosslinking, acrylic emulsion available from Rohm and Haas Company, Philadelphia, Pa., and 1 percent Velvetol CHR a cationic quaternized imidazoline available from Quaker Chemical Corporation, Conshohocken, Pennsylvania. Noble and Wood handsheets prepared from this furnish had the following physical properties:

Basis weight	10.7
Tensile strength	52.4
Fold value	658
Crush value	358

By comparison handsheets prepared from a pulp sample which had not been treated with the chemical additives had the following physical properties:

Basis weight	10.7
Tensile strength	62.7
Fold value	1072
Crush value	7458

Example VIII

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleached Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5 minute intervals - 0.75 percent Quaker 2000, and 5.0 percent Rhoplex P339. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.0
Tensile strength	6.1
Fold value	183
Crush value	60

By comparison sheets prepared from a pulp treated only with 0.75 percent Velvetol 2000 had the following physical properties:

Basis weight	11.1
Tensile strength	2.3
Fold value	183
Crush value	28

And sheets prepared from a sample of untreated pulp had the following physical properties:

Basis weight	11.1
Tensile strength	11.8
Fold value	357
Crush value	146

Example IX

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleached Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5

minute intervals - 0.45 percent Resin S 243, 9.0 percent Tylac RB 1118, an anionic, carboxylated styrene butadiene latex containing approximately 50 percent styrene, available from Standard Brands Chemical Corporation, Dover, Delaware, 0.09 percent Resin S 243, and 0.25 percent Quaker 2000. Handsheets prepared from this pulp had the following properties:

Basis weight	10.0
Tensile strength	4.9
Fold value	183
Crush value	50

By comparison handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.0
Tensile strength	9.9
Fold value	312
Crush value	142

Example X

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleaching Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5 minute intervals - 0.15 percent Lufax 295, 5.0 percent Rhoplex P339, 0.01 percent Lufax 295, and 0.25 percent dialkylamide diethyl ammonium sulfate. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.7
Tensile strength	9.2
Fold value	255
Crush value	70

By comparison handsheets prepared from a sample of the pulp treated only with 0.25 percent dialkylamide diethyl ammonium sulfate had the following physical properties:

Basis weight	10.6
Tensile strength	4.9
Fold value	195
Crush value	58

Handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.6
Tensile strength	9.3
Fold value	267
Crush value	94

Example XI

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleaching Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals, added sequentially at 5 minute intervals - 0.15 percent Lufax 295, 5.0 percent Rhoplex P339, 0.01 percent Lufax 295 and 0.25 percent dihydrogenated tallow dimethyl ammo-

nium chloride. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.3
Tensile strength	7.6
Fold value	240
Crush value	62

By comparison handsheets prepared from a sample of the pulp treated only with 0.25 percent dihydrogenated tallow dimethyl ammonium chloride had the following physical properties:

Basis weight	10.0
Tensile strength	3.5
Fold value	156
Crush value	48

Handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.3
Tensile strength	10.5
Fold value	336
Crush value	117

Example XII

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleaching Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5 minute intervals -- 0.20 percent Lufax 295, 5.0 percent Rhoplex P339 and 0.50 percent sodium tetradecyl sulfate. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.4
Tensile strength	8.6
Fold value	216
Crush value	57

By comparisons, handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.5
Tensile strength	11.6
Fold value	372
Crush value	161

Example XIII

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleaching Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5 minute intervals -- 0.20 percent Lufax 295, 5.0 percent Rhoplex P339 and 0.50 percent of the sodium salt of sulfated nonyl phenoxy poly(ethylene oxy) ethanol. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.5
Tensile strength	7.0
Fold value	184
Crush value	51

By comparison, handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.5
Tensile strength	11.6
Fold value	372
Crush value	161

Example XIV

A wood pulp furnish was prepared, as in Example I, comprising 60 percent bleached Kraft softwood and 40 percent bleached Kraft hardwood. A sample of the pulp, in a Hobart Mixer operating at 60 rpm, was treated with the following chemicals added sequentially at 5 minute intervals -- 0.15 percent Lufax 295, 5.0 percent Rhoplex P339, 0.01 percent Lufax 295 and 0.25 percent Rycofax 637, an amphoteric quaternary ammonium compound available from Reichold Chemicals, Inc., White Plains, New York. Handsheets prepared from this pulp had the following physical properties:

Basis weight	10.5
Tensile strength	8.8
Fold value	239
Crush value	74

By comparisons, handsheets prepared from a sample of the untreated pulp had the following physical properties:

Basis weight	10.5
Tensile strength	11.6
Fold value	372
Crush value	161

What is claimed is:

1. In a method of producing a water-laid cellulosic sheet material, the improvement which comprises adding to a slurry comprising cellulosic fibers; a cationic surface active agent as a debonder; at least one anionic or nonionic resin selected from the group consisting of acrylic emulsions and anionic styrene butadiene latexes; and a deposition aid for the resin in which the deposition aid, the resin and the debonder are sequentially added to the furnish and then forming a cellulosic sheet from said slurry.

2. A method, as claimed in claim 1, in which the resin in the furnish is a nonionic acrylic emulsion.

3. A method, as claimed in claim 1, in which the resin in the furnish is an anionic styrene butadiene latex.

4. A method, as claimed in claim 3, in which the latex is a carboxylated styrene butadiene.

5. A method, as claimed in claim 1, in which the cellulosic fibers are wood pulp fibers.

6. A method, as claimed in claim 1, in which the cellulosic fibers are a combination of wood pulp fibers and synthetic fibers.

7. A method, as claimed in claim 6, in which the synthetic fibers are rayon fibers.

8. A method, as claimed in claim 1, in which a quaternized imidazoline is added to the furnish as a deposition aid for the resin.

9. A method, as claimed in claim 1, in which the cationic surface active agent in the furnish is a quaternary ammonium compound.

10. A method, as claimed in claim 9, in which the quaternary ammonium compound is an imidazoline.

11. A method, as claimed in claim 9, in which the quaternary ammonium compound is an alkyl ammonium salt.

12. A method, as claimed in claim 1, in which the deposition aid is a vinyl imidazoline polymer.

13. A method, as claimed in claim 1, in which the amount of resin in the furnish is equal to from about 3.0 to about 15.0 percent of the oven-dry weight of the fibers employed.

14. A method, as claimed in claim 1, in which the amount of debonder is equal to from about 0.15 to about 2.0 percent of the oven-dry weight of the fibers employed.

15. A method, as claimed in claim 1, in which the amount of deposition aid is equal to from about 0.1 to about 3.0 percent of the oven-dry weight of the fibers employed.

16. A method, as claimed in claim 8, in which the amount of deposition aid employed is equal to from about 0.1 to about 3.0 percent of the oven-dry weight of the fibers employed.

17. A method, as claimed in claim 8, in which the furnish comprises wood pulp fibers, a cationic surface active agent, a deposition aid for the resin, and an anionic acrylic emulsion.

18. A method, as claimed in claim 1, in which the debonder is added to the slurry prior to the addition of the deposition aid and the resin.

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