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**FLEXIBLE PAPER WEB AND PROCESS OF
PRODUCING SAME**

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No Drawing. Application July 16, 1953
Serial No. 368,515

16 Claims. (Cl. 162-165)

This invention is concerned with new and improved methods of incorporating polymeric materials from colloidal dispersion onto fibers prior to sheet formation.

Incorporation of polymers into fibrous webs of cellulosic or other fibers in itself is old. Incorporation of rubbers, bitumens, or resins into paper or felt by saturation of the previously prepared web in order to improve physical characteristics has been practiced for many years. The disadvantages of this method of preparing sheets containing both fibers and polymer are:

(A) The type of sheet is limited to one which can be penetrated readily by the often viscous saturating media, and

(B) Saturation constitutes an often costly and complicated process requiring removal of the media from which the polymer is applied, usually by heat. If aqueous media are used, as is usual, a wet, water weakened sheet must be handled involving the hazard of loss of material due to tears or breaks, or, if organic solvent media are involved, handling of flammable and, in many cases, toxic or explosive solvents is required.

In recent years many attempts have been made to incorporate the required polymer onto the fibers prior to actual sheet formation. These processes were concerned primarily with incorporation of rubber or rubber-like polymers from latices or dispersions, in amounts up to about forty percent by weight of the fiber, and in subsequent felting of the treated or coated fibers into a sheet on a paper machine.

Although by previously known methods incorporation of more than forty percent of the fiber weight of rubbery polymer is possible, treatment to obtain higher polymer contents is commercially impractical by these methods. This is due particularly to difficulties with sheet formation and to the impossibility of running for more than short periods without stopping to clean the paper machine.

Paper is made by preparing a slurry of cellulose fibers in water, felting the fibers together by draining away part of the water on a porous screen, and removing water not lost through drainage by pressing and drying the wet sheet. The slurry of fibers in water is known as stock, and the addition of polymers, in suitable water dispersion or solution, to the stock and causing the polymer to adhere to the fibers constitute what is known as beater impregnation, although such additions may be made to the stock at any point in the system prior to sheet formation.

By far the greatest interest in beater impregnation relates to incorporation of rubber or rubber-like synthetic polymers into paper. These polymers are readily available in the form of aqueous anionic colloidal dispersions. While saturation of a finished paper sheet with such dispersions is possible, for practical saturation speeds and efficiencies an open, porous sheet of paper is required in order to obtain penetration, and a sheet containing some wet strength is usually needed to minimize losses due to tears, breaks, and uneven stretching. Incorporation

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tion of up to forty percent of the fiber weight of some synthetic rubber-like polymers by beater impregnation yields products of interest in fields requiring saturated papers of not too critical physical requirements, for instance in the fields of shoe cover stocks and light duty gasket stocks. However, high rubber content is necessary for applications of impregnated paper requiring maximum unification of the paper, as for instance in the making of backings for pressure-sensitive adhesive tape. Substantially greater resistance to delamination is obtainable by this process with the maximum amount of rubber-like polymer than can be obtained by previously known methods of beater impregnation. To the extent of applicants' knowledge with the exception of the process disclosed in U.S. patent application Serial Number 210,282, filed February 9, 1951, by Dr. C. L. Weidner and I. R. Dunlap, prior art processes of beater impregnation involved coagulation of water dispersions of rubbery polymers by addition of aluminum sulfate, or acid, or the use of an acidic colloidal polymer. In all these cases coagulation required the use of acidic media at some step. The amount of polymer that could be incorporated by these methods was limited, and the type of polymer was limited to minimum Mooney plasticities of about fifty. In U.S. patent application Serial Number 210,282, the use of water soluble N-basic polymers is disclosed for precipitation of latices onto papers or other fibers. The use of acid is also unnecessary in connection with the process of this application.

The objects of the present invention are as follows:

(A) To incorporate greater amounts of polymers, especially rubber-like polymers, onto fibers than has been possible under the prior art and to do so with greater efficiency.

(B) To obtain a sheeted, or felted, product of greater strength and uniformity than was possible by similar means previous to this invention.

(C) To incorporate polymeric materials prior to sheet formation which are of such a nature that they could not be so incorporated by previously known methods.

(D) To obtain, at lower ratios of polymer to fiber weight, sheets equivalent in physical tests to latex saturated paper.

It has now been found that co-precipitation of water-soluble or water-dispersible resins of the type represented by alkali-catalyzed phenol-formaldehyde polymers and synthetic rubbery polymers under neutral or basic conditions onto fibers by means of the poly-N-basic compounds presents marked advantages. This is true particularly as are concerned sheet formation, polymer retention, and ease of operation, particularly when soft polymers are employed. The precipitating action of poly-N-basic compounds takes place under all types of conditions and operations on any hydrophobic colloid at almost any hydrogen ion concentration. It has been found that these poly-N-basic compounds also precipitate, very efficiently, water soluble or water dispersible resins of the phenol-formaldehyde type from aqueous solution or dispersion. These resins are soluble or dispersible only in alkaline media. Co-precipitation of resins of this type under non-acidic conditions with any of the widely available anionic dispersions of synthetic rubbers or rubber-like polymers onto fibers yields sheets surpassing any product or process previously known in physical properties, ease of paper machine operation, and retention of polymer.

This invention involves co-precipitation of a hydrophobic rubbery polymer from aqueous alkaline colloidal dispersion and water-soluble or water-dispersible phenol-formaldehyde resin, condensed under alkaline conditions from aqueous solution or dispersion onto fibers from an

anionic water dispersion in a pH range above about seven. The phenol-formaldehyde resin may amount to from about one to about twenty-five percent by weight of the rubbery polymer selected, and the amount of combined polymer may be from a fraction of one percent to more than one hundred percent of the weight of the polymer. The water-dispersed fibers comprise from about 0.05 to about three percent of the total weight of the dispersion. Water-dispersible phenol-formaldehyde resin for purposes of this invention includes only those resins that are dispersible without the aid of dispersing agents other than those formed during the condensation of the resin.

In carrying out the invention it has been found convenient to prepare a mixed dispersion containing the hydrophobic polymer and the resinous, hydrophilic polymer. This is accomplished by adding a water solution or dispersion of the phenolic resin to diluted and stabilized commercial latex. The desirable degree of latex dilution will vary with the amount to be added to the fibers, the nature of the dispersion and the ratio of resinous to rubbery polymer to be used. The addition of the water-soluble polymer should take place at a pH above that at which the anionic colloid would be unstable, usually at a pH of from about 6.5 to about 8.5.

In the execution of the invention we find most advantageous for precipitation certain poly-N-basic compounds disclosed in U.S. patent application Serial Number 210,282, filed February 9, 1951, by Charles Leslie Weidner and Isaac Richard Dunlap. Particularly preferred are the reaction products of a guanidine in accordance with that patent application. By "a guanidine," guanidine or any of its salts is meant. The guanidine reaction product may be added to the extent of from about five to about fifteen percent of the combined weight of the hydrophobic and hydrophilic polymer present in the aqueous medium.

In a typical case, a commercial acrylonitrile-butadiene copolymer latex received from the factory at 38.8 percent by weight of solids was diluted to twenty percent solids by addition of water containing one percent by weight, based on the polymer solids, of potassium rosinate. After thorough stirring of the diluted latex, a twenty percent by weight solution of the phenolic resin in water at a pH of 8.2, representing one-tenth the weight of acrylonitrile-butadiene solids in the diluted latex, was added under stirring.

In many instances it is advantageous to age the dispersion containing the resinous and rubber-like polymers for twenty-four hours or more before use.

In addition to wide applicability to various types of polymers, the poly-N-basic precipitation process as disclosed herein permits use of polymers of softer and more sticky nature than was practical under the prior art. In prior art processes involving acidic media, the resulting polymer coated fibers were quite sticky and exhibited a marked tendency to adhere to each other and to any surface with which they came in contact—machine, wire, press rolls, or paper machine felt. The process uses precipitation under neutral or basic conditions and preserves the dispersing agent, which would be destroyed by the action of acid and thus plasticize and make more sticky the precipitated rubber.

This process makes usable butadiene polymers of as low as 19 Mooney plasticity with one hundred percent retention of polymer on the fiber and with good formation of the sheet and no sticking or fouling of paper machine parts such as take place when acidic precipitation processes are used.

An advantage of operation under non-acidic conditions, with consequent preservation of the latex dispersing agent, is that sheets containing rubbery polymer incorporated by our process of beater impregnation may be repulped easily and economically in conventional equipment. This re-use of broke, which is impossible with previously known processes, makes possible the economical salvaging of the off-weight, wrinkled, and torn product of start-

ing-up of the paper machine, with consequent saving of valuable fiber and polymer.

Still another advantage is the greater ease of treatment of the paper stock after precipitation with our invention than is possible under the prior art.

The phenolic type resin is limited to those which are water soluble or water dispersible. We have found that suitable resins of this type for our process may be prepared with a molar ratio of formaldehyde to phenol of from about one to about two and one-fourth. The ratio of water-soluble or water-dispersible resin to hydrophobic anionic dispersed polymer may be varied widely. Practical limits of stability of the mixed dispersion require that the ratio of resinous to rubbery polymer be not greater than about one to four on a weight of solids basis. However, any ratio of one component to the other may be used if mixing is immediately before addition to the paper stock, or mixing of components may be carried out in the presence of the fiber in the paper machine system. The most desirable ratio of resinous to rubbery polymer for beater impregnation in applications competitive with latex saturated papers is about one to ten. At this ratio the influence of the resin on sheet formation and operation of the paper machine is approximately at a maximum and there is a minimum of stiffening of the sheet. However, any ratio of resinous to rubbery polymer is contemplated.

The type of polymer applied from colloidal dispersion is limited only to those from which an anionic dispersion can be prepared. Any of the usually available synthetic rubbers such as copolymers of styrene and butadiene, or of acrylonitrile and butadiene, or copolymers and polymers of chlorobutadiene, acrylates, styrene, vinyl chloride, Factice or polyvinyl acetal-type polymers may be used in practicing this invention when used as anionic aqueous dispersions.

As stated above, basic catalyzed phenolic resins of formaldehyde to phenol ratio of from about one to about two and one-fourth moles of formaldehyde per mole of phenol may be used. Substituted phenols such as resorcinol or cresol may also be used when suitably reacted with formaldehyde to yield water-soluble or water-dispersible polymeric material.

The fibers onto which the dispersed polymers are precipitated may be of any type. The precipitation process operates with equal efficiency with any cellulosic fiber whether subject to hydration (kraft, sulphite, etc.) or not (rayon). It also operates with such organic non-cellulosic fibers as nylon and acrylic polymer fibers and with inorganic fibers such as glass and asbestos.

In the co-pending application, impregnation was defined as the incorporation of more than ten percent of the fiber weight of polymer prior to sheet formation. This application is concerned primarily with the incorporation of amounts of polymer greater than about twenty percent by weight of fiber weight, but the incorporation of from a fraction of one percent to more than one hundred percent by the methods disclosed is possible and is contemplated. The optimum amount and type of polymer mixture on any given fiber is determined by the use anticipated for the finished sheet. In general, soft polymers yield sheets of greater tear and lesser tensile strength than an equivalent amount of a harder polymer mixture.

As a beater impregnated backing for pressure-sensitive tape, a sheet comprising about 62.5 percent by weight of kraft fiber and 37.5 percent by weight of a polymer mixture comprising ninety percent by weight of a copolymer of acrylonitrile and butadiene (forty percent acrylonitrile, sixty percent butadiene by weight), and ten percent by weight of a water-dispersible phenolic resin made by reacting one mole of phenol with one and seventy-five hundredths of a mole of formaldehyde, using five hundredths of a mole of sodium hydroxide as a catalyst, is preferred.

In general, the amount of poly-N-basic compound required to precipitate the mixture of rubber-like and resinous polymers onto fibers with one hundred percent efficiency (all of polymer fixed to fiber) is ten percent or less of the dry weight of polymer to be precipitated. However, the necessary quantity may be as low as one percent or as high as twenty percent by weight of the polymer to be precipitated, depending upon consistency of the pulp-polymer slurry at the time of precipitation. An excess of precipitating agent is not harmful; an inadequate amount will result in loss of polymer in white water. Other than the above factor of amount of precipitating agent required, the precipitation step may be carried out at any convenient pulp consistency at any point in the paper machine stock system.

Temperature of stock at the time of precipitation is not critical—the operation has been carried out at as low as thirty-four degrees Fahrenheit and as high as one hundred and forty degrees Fahrenheit with equal effectiveness. No aging of the stock is required after the addition of the precipitating agent, and if further refinement of the stock after precipitation of the polymer is desired, a reasonable degree of refining may be carried out without detrimental effect on the retention of polymer by the stock.

The distinguishing characteristics of our invention are:

(A) Co-precipitation of a water-soluble or water-dispersible resinous and a hydrophobic polymer from anionic colloidal dispersion.

(B) Carrying out precipitation operation under neutral or alkaline conditions in the presence of fibers.

The invention is further illustrated by the following examples:

Example I

The following table illustrates the advantage to be gained by co-precipitation of rubbery polymer and phenolic resin under non-acid conditions as described in the preparation of beater impregnated papers over similar precipitation of the rubbery polymer alone. All sheets contained thirty-seven and one-half percent by weight of polymer based on the weight of sheet. Fibers of 750 cc. Schopper Riegler freeness of weight equivalent to a thirty-pound sheet (24 x 36 x 480) was contained in all the samples. Retention was quantitative with all samples as shown by clear white water.

Polymer	Tensile, lbs./in.	Formation
50 Mooney plasticity 60-40 butadiene acrylonitrile.	22.5	Good to excellent.
Above plus 10 percent phenolic resin.	23.2	Excellent.
50 Mooney plasticity 75-25 butadiene acrylonitrile.	16.3	Good.
Above plus 10% phenolic resin.	24.9	Excellent.
Type IV, G.R.S.	19.6	Fair to good.
Above plus 10% phenolic resin.	21.2	Good.
Polychloroprene plus 10% phenolic resin.	19	Do.
High vis. polyvinyl butyral.	20.6	Do.
Above plus 10% phenolic resin.	24.0	Excellent.

Note.—The phenolic resin used was a water-dispersible commercial product, obtained as a 65% solution in water at a pH of 8.5-9.

Example II

This example illustrates the effect of variation in resin to rubber ratio in the carrying out of our invention. The samples differed only in ratio of phenolic resin to rubbery polymer. Sheet weight, processing and retention were as outlined in Example I above. The rubbery polymer was a butadiene-acrylonitrile copolymer of 60-40 monomer ratio with a Mooney plasticity of about fifty, and the phenolic resin was the commercial product described in Example I.

The following table gives the results obtained by varying the ratio of phenolic resin in the polymer content of the sheet from zero to twenty percent by weight of the nitrile rubber.

Percent resin	Tensile, lbs./in.	1 ply 400 cc. Gurley density, min.
0	22.5	2.8
5	21.4	17.75
10	20.4	18.2
15	21.0	22.0
20	22.8	22.0

The variation in air permeability as measured by Gurley densometer is regarded as more indicative of sheet quality than the slight variation in tensile strength noted, since it is a measure of the important property of delamination resistance or internal bonding strength.

Example III

This example illustrates the effect of variation in phenol to formaldehyde ratio in the resin used in carrying out the invention. All the resins listed below were prepared by heating the reactants in the mole ratio indicated with a minor amount of sodium hydroxide as catalyst. The rubbery polymer component was the acrylonitrile rubber used in Example II. Sheet weight and level of treatment were also as described in Example II.

Mole ratio HCHO to phenol	Tensile, lbs./in. width	1 ply 400 cc. Gurley density, min.
1-1	19.6	7.8
1.25-1	19.1	10.25
1.5-1	21.0	8.16
2-1	22.1	8.0
2.25-1	20.4	19.0

Example IV

The following table shows tensile strength and drain time in a standard T.A.P.I. sheet mold of hand sheets based on thirty pounds (24 x 36 x 480) fiber treated with from twenty to one hundred and twenty percent of the fiber weight of the nitrile rubber used in Example II combined with zero, five and ten percent of the phenolic resin on the weight of the rubber described in the above example. All hand sheets were prepared in the same manner and contained the same weight of fiber which had been beaten to 700 cc. Schopper-Riegler freeness.

Treatment	Tensile, lbs./in.	Drain time, sec.
None	17.6	6.7
20%—10% resin in polymer	19.9	8.5
40%—10% resin in polymer	23.0	12.1
60%—10% resin in polymer	22.0	10.5
75%—10% resin in polymer	22.5	10.7
55 100%—10% resin in polymer	21.4	6.0
120%—10% resin in polymer	20.0	6.5
20%—5% resin in polymer	19.2	9
40%—5% resin in polymer	18	9.1
60%—5% resin in polymer	20.6	10.0
75%—5% resin in polymer	20.6	8.5
100%—5% resin in polymer	22.7	7.1
120%—5% resin in polymer	20.4	7.1
60 20%—No resin in polymer	24.0	7.7
40%—No resin in polymer	24.6	7.4
60%—No resin in polymer	18	6.1
75%—No resin in polymer	18.6	6.2
100%—No resin in polymer	12.9	5.8
120%—No resin in polymer	10.8	5.7

It might be pointed out here that drain time is important in two respects, as an indication of how the stock will lose water on a paper machine wire, and in so doing effect sheet formation. A free stock losing water too readily would be expected to yield a sheet of uneven, wild formation, while a slow stock might limit production speed to a prohibitive extent.

Example V

The previous example shows in tensile strength and

drain time one of the processing advantages of the invention. This example illustrates a difference in refining characteristics of the preferred rubbery-resinous blend of polymers described in Example II, precipitated according to this and our previous application, and similarly precipitated rubbery polymer alone, with both the resinous-rubbery composition and rubber precipitated by alum.

The pulp on which the polymer and polymer composition was precipitated was a spruce kraft at 750 cc. Schopper-Riegler freeness, and the composition treated comprised 60% by weight of polymer on the fiber weight. A Waring Blender was used as refining medium with a fixed current source.

PRECIPITATION ACCORDING TO THIS INVENTION

Preferred resinous-rubbery Composition	Rubbery polymer—No resin
No refining, 850 cc. S.R.	No refining, 850 cc. S.R.
1.5 min. refining, 820 cc. S.R.	1.5 min. refining, 820 cc. S.R.
3.0 min. refining, 800 cc. S.R.	3.0 min. refining, 820 cc. S.R.
15.0 min. refining, 790 cc. S.R.	15.0 min. refining, 820 cc. S.R.

ALUM PRECIPITATED

No refining, 860 cc. S.R.	No refining, 880 cc. S.R.
1.5 min. refining, 850 cc. S.R.	1.5 min. refining, 900 cc. S.R.
3.0 min. refining, 850 cc. S.R.	3.0 min. refining, 880 cc. S.R.
15 min. refining, 770 cc. S.R.	15 min. refining, 850 cc. S.R.

Thus equivalent treatment (3 min.) brought about a reduction in freeness of 50 cc. for the resin-rubber treated pulp when prepared by our invention, compared with a reduction of only 10 cc. when the same composition was precipitated with alum. When the rubbery polymer alone was used, the same treatment yielded a reduction of 30 cc. with our invention and none when the rubbery polymer was precipitated with alum.

Example VI

This example illustrates the use of broke from the disclosed process.

Five hundred grams of air dry paper from a machine run based on sixty percent treatment of kraft fiber with a mixture of ninety percent acrylonitrile-butadiene copolymer of 60-40 monomer ratio, 50 Mooney plasticity, and ten percent phenolic resin, as previously disclosed in Example I, was torn into small pieces and placed with twenty liters of cold water in a one-pound Valley beater. After five minutes of circulation without pressure, 3,500 grams was placed on the bed plate and the operation continued for ten minutes.

The following table shows physical test values obtained when varying percentages of the above defibered broke was mixed with fresh treated fiber and formed into 47 lbs./in. weight sheets.

Percent broke	Tensile strength, lbs./in.	Gurley density, sec.
100	21.5	480
50	22	450
0	22	490

Example VII

This example discloses the preparation of guanidine-formaldehyde condensation products used as the co-precipitating agent in accordance with the present invention.

One hundred and twenty-one grams commercial guanidine carbonate and one hundred grams commercial thirty-seven percent formaldehyde were mixed and heated, with occasional stirring, on an electric hot plate.

The initial hydrogen ion concentration of the mixture was equivalent to a pH of about 8.5. At the end of four hours of heating, the reaction vessel contained a

viscous (when hot) transparent mass and the hydrogen ion concentration had fallen to a pH of about 7.5. Water was added and stirred to dissolve the reaction product. All during the heating, there was evolution of carbon dioxide from the reaction, and it was to facilitate escape of this material that water was added. After additional heating at the boiling point of the solution for one and one-half hours, the pH was about 7.2 as measured with pH paper, and heating was discontinued.

The product obtained was an almost colorless solution containing thirty-seven percent solids. The viscosity of this thirty-seven percent solution was not substantially greater than that of water. The dry reaction product was a transparent, very slightly colored, solid, having a softening point below eight degrees centigrade.

Heating of the reaction mixture more strongly than was done in the above example by allowing substantially all the water to evaporate from the reaction components yields a light yellow, somewhat brittle solid with a softening point above one hundred degrees centigrade. Heating the reactants in the above proportions on a steam plate yielded, upon heating for about ten hours, a product having a softening point below room temperature which was colorless and transparent.

The reaction products obtained in the examples given above were substantially equivalent in precipitating power when used as described in this disclosure; yet, neither guanidine carbonate nor formaldehyde alone or in combination in an unreacted condition have significant precipitating action unless used or added in concentrations much greater than is required for their reaction product as described above.

The product we desire to use is a water-soluble condensation polymer of guanidine and/or its carbonate and formaldehyde. The above examples are based on the use of commercial materials, and some variation may be expected due to slight differences in materials or reaction conditions. The above is given by way of example only since an equivalent product might be obtained with somewhat different ratios of reactants by control of reaction conditions.

In formation of one of our preferred precipitating agents, guanidine carbonate may be mixed with urea, in molar ratios of from about one mol of guanidine salt to about one and one-third mols of urea, and the resulting mixture reacted with formaldehyde at steam bath temperature until clear to form a product useful in the practice of this invention. Even high ratios of urea to guanidine salt may be used if sufficient control of reaction conditions is used to yield a product soluble in water on dilution to low solids.

Similarly to the above, but at lower ratios thiourea may be employed as a co-reactant with the guanidine salt. However, if more than one mol of thiourea per two and one-half mols of guanidine salt is used, difficulty in obtaining a water-soluble product after resinification is encountered.

The claims are:

1. A process of producing felted, fibrous webs, comprising the steps of mixing with a water dispersion comprising from about 0.05 to about 3 percent by weight of fiber, an anionic colloidal dispersion of a hydrophobic rubbery polymer and an alkaline hydrophilic condensation product of a phenol with formaldehyde in an aqueous medium, said phenol condensation product being dispersible in water without the aid of dispersing agents other than those formed in said condensation; precipitating said hydrophobic and hydrophilic polymers onto said fibers under non-acid conditions by addition of the organic water-soluble polymer formed by reacting a guanidine compound selected from the group consisting of guanidine and the water soluble salts of guanidine with formaldehyde under basic conditions; and subsequently forming a web at a pH within the range in which the anionic colloidal dispersion is normally stable.

2. A process for producing felted fibrous webs comprising the following steps carried out at a pH of from about 6.5 to about 8.5: adding to a dispersion of fiber in water comprising from about 0.05 to about 3 percent fiber by weight of the dispersion, an aqueous anionic dispersion of a copolymer of acrylonitrile and butadiene comprising a major proportion of butadiene, mixed with a water-dispersible alkaline condensation product in an aqueous medium of phenol with formaldehyde, said mixture comprising at least 5 percent by weight of said copolymer; precipitating said copolymer and said condensation product onto said fibers under non-acid conditions by addition of from about 5 percent to about 15 percent by weight of the combined weight of said polymer and condensation product of a water-soluble cationic reaction product under basic conditions of a guanidine compound selected from the group consisting of guanidine and the water soluble salts of guanidine with formaldehyde; and forming a felted fibrous web from the combined fiber and polymer.

3. The process of claim 2, including the step of aging the copolymer-phenol formaldehyde condensation product dispersion prior to precipitation.

4. The process as defined in claim 2, wherein said fiber is paper fiber.

5. The process as defined in claim 2, wherein said fiber is kraft paper fiber.

6. A process as defined in claim 2, wherein the guanidine of the reaction product is guanidine carbonate.

7. The process of claim 2, wherein from about ten to about one hundred percent by weight of polymeric components are incorporated into the web based on the weight of the fiber.

8. The process of claim 2, wherein from about one to about twenty percent by weight of the cationic reaction product are used based on the weight of the material to be precipitated.

9. The process of claim 2, wherein the ratio of phenol formaldehyde condensation product to copolymer is less than about one to four.

10. A process in accordance with claim 9, wherein the ratio is about one to ten.

11. A process for producing felted fibrous webs comprising the steps of adding to a dispersion of a fiber in water composed of from about 0.05 to about 3% fiber by weight of the dispersion, an aqueous anionic dispersion of a copolymer of acrylonitrile and butadiene comprising a major proportion of butadiene, mixed with a water-dispersible alkaline formaldehyde condensation product, said mixture comprising at least 5% by weight of said copolymer; precipitating said copolymer and said condensation product onto said fibers under non-acid conditions by addition of from about 5% to about 15% by weight of the combined weight of said polymer and formaldehyde condensation product of a water-soluble cationic reaction product under basic conditions of a guanidine compound selected from the group consisting of guanidine and the water-soluble salts of guanidine with formaldehyde; and forming a felted fibrous web from the combined fiber and polymer.

12. The process as defined in claim 11 wherein from about 10 to about 100% by weight of polymeric components are incorporated into the web based on the weight of the fiber.

13. A process as defined in claim 12 wherein the ratio of said formaldehyde condensation product to said copolymer of acrylonitrile and butadiene is less than about 1:4.

14. A flexible felted fibrous paper web comprising a paper fibrous sheet, a mixture of a hydrophobic rubbery polymer and hydrophilic formaldehyde condensation product incorporated in said sheet so as to unify and internally bond said sheet, said polymer comprising about 10 to about 100% by weight based on the weight of the fiber, and the ratio of said formaldehyde condensation product to said polymer being less than about 1:4; said web characterized by high receptivity to saturation by water and aqueous impregnants and exhibiting enhanced delamination resistance, internal bonding strength and tensile strength.

15. A flexible felted fibrous paper web comprising a paper fibrous sheet, a mixture of a hydrophobic rubbery copolymer of butadiene and acrylonitrile composed of a major proportion of butadiene and a hydrophilic formaldehyde condensation product incorporated in said sheet so as to unify and internally bond said sheet, said copolymer comprising about 10 to about 100% by weight based on the weight of the fiber and the ratio of said formaldehyde condensation product to said copolymer being less than about 1:4; said web characterized by high receptivity to saturation by water and aqueous impregnants and exhibiting enhanced delamination resistance, internal bonding strength and tensile strength.

16. A flexible felted fibrous paper web comprising a paper fibrous sheet, a mixture of a hydrophobic rubbery copolymer of butadiene and acrylonitrile composed of a major proportion of butadiene and a hydrophilic phenol-formaldehyde condensation product incorporated in said sheet so as to unify and internally bond said sheet, said copolymer comprising about 10 to about 100% by weight based on the weight of the fiber and the ratio of said phenol-formaldehyde condensation product to said copolymer being less than about 1:4; said web characterized by high receptivity to saturation by water and aqueous impregnants and exhibiting enhanced delamination resistance, internal bonding strength and tensile strength.

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