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CHEMICAL PROCESS AND PRODUCT

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This invention concerns methods of producing felted fibrous webs and the products resulting therefrom. More particularly it is concerned with methods for producing such webs comprising, in addition to the fiber, non-fibrous material affixed to the fiber prior to or during web formation. While the invention has particular utility in the paper making field, it is applicable to the formation of fibrous webs other than paper. The invention is most important for affixing polymeric materials, and particularly polymers having average particle size smaller than natural rubber latex, but it may be used also to affix particles of rubber latex and in fact particles of widely diversified solid substances, whether polymeric or non-polymeric, organic or inorganic.

Webs comprising fibrous and non-fibrous material may be produced by either of two methods: (*a*) Saturation of a previously formed web with a dispersion or solution of the fibrous material; (*b*) Precipitation of non-fibrous material onto the fiber prior to web formation.

Both the above methods of the prior art have certain limitations; saturation involves the use of equipment for removal of the medium from which the non-fibrous material was applied and is limited to open, porous webs which can be penetrated by the often viscous saturating media.

Precipitating of non-fibrous material from water dispersion onto the fibers, known as beater impregnation although precipitation may be at any time prior to sheet formation, has the disadvantages of requiring complete precipitation, of frequent formation difficulty, of foam problems or operation under acid conditions which yields a non-usable broke containing appreciable quantities of non-fibrous material.

Previous U. S. applications in which the inventor was an applicant, U. S. Serial Numbers 210,281 and 210,282, filed February 9, 1951 and S. N. 368,515, filed July 16, 1953, of which applications this application is a continuation in part, disclose the use of poly-N-basic water-soluble organic polymers to bring about precipitation of water dispersions of non-fibrous material such as rubber-like polymers onto pulp fibers. These applications disclose processes and materials which overcome to a large extent the disadvantages of the prior art of beater impregnation, yielding, with one hundred percent retention of the non-fibrous material in the sheet, products of good to excellent formation with an easily re-pulped broke. However, on paper machines not designed specifically for foamy stocks a foam problem has been encountered sometimes at fairly high levels of treatments. Control of foam with antifoam reagents was possible and practical in the production of flat papers or papers comprising only minor amounts of rubbery polymer, but the use of antifoam reagents in attempting to produce creped webs comprising more than approximately ten percent rubbery polymer prevented sticking to the press roll or Yankee drier, and it was impossible to crepe.

In accordance with this invention, precipitation takes

place in presence of the poly-N-basic compounds disclosed in the above mentioned earlier applications, in presence of calcium, barium, strontium and/or magnesium ion, or any of their combinations, and at least one type of anion, forming water-soluble salts with said metal ions. Precipitation in this manner yields a non-foaming stock with substantially all the dispersed material retained on the fiber, a product of excellent formation, and an easily re-usable broke. Surprisingly, a great lessened quantity of poly-N-basic polymer is required to bring about complete precipitation of a given weight of dispersed polymer than is required in absence of the metal salt.

No fundamental explanation of the action of the mixed precipitating agent can be offered. Used without the poly-N-basic salt, the water-soluble salt of the metal in small amounts will bring about precipitation of the major portion of the colloidally dispersed material, but it is often impossible to precipitate the last traces of dispersed material by the addition of inorganic salt. As previously disclosed, the addition of poly-N-basic organic compound as a salt will precipitate completely the dispersed material in a colloid system when added in an amount equal to, under the usual paper making conditions, for instance about five percent by weight of the weight of the dispersed material.

Any of the poly-N-basic compounds as salts or adapted to form salts disclosed in the previous applications, U. S. 210,281, U. S. 210,282 and U. S. 368,515, may be used with water soluble salts of Group II metals such as calcium, barium, strontium or magnesium. The preferred poly-N-basic compounds are the salt forming reaction products of guanidine and aldehyde, and preferably guanidine formaldehyde. The ratio of metal ion to reaction product of guanidine and aldehyde may be from about one-tenth of one mol to about ten mols of alkaline earth metal per mol of reaction product. The preferred ratio is from about two-tenths of one mol to about seven-tenths of one mol of alkaline earth metal ion per mol of reaction product of guanidine and aldehyde.

It is preferred that the hydrgen ion concentration at precipitation be above about 5.5, and, for best freedom from foam, under nine. Best results are obtained at a pH of from about six to about eight.

The preparation of the mixed precipitating agent involves only the addition of a water solution of the metal salt to a similar solution of the poly-N-basic salt. As an alternative method of preparation, the hydroxide of the Group II metal may be used to control the pH during the reaction of guanidine salts such as the nitrate (which yields an acid solution in water) with formaldehyde, as disclosed in U. S. 210,282, and the resulting product comprising the mixture of organic and inorganic salt used in the practice of this invention without further treatment or purification.

This invention is practical and operable with dispersions made with anionic, cationic or non-ionic dispersing agents as disclosed in previous U. S. applications 210,281, 210,282 and 368,515. It is further illustrated in its preferred forms by the following examples.

Example I

To two liters of commercial thirty-seven per cent formaldehyde was added two kilograms of guanidine nitrate and one hundred grams of calcium hydroxide and the whole heated to gentle boiling. After thirty minutes of such heating, the pH of the solution had dropped to approximately 5.5, and a further addition of one hundred grams of calcium hydroxide was made and stirred into the hot solution. After thirty more minutes a third addition of fifty grams of calcium hydroxide was made.

After stirring this last addition, heating was stopped and the mixture allowed to cool. Total solid matter, guanidine resin and calcium salt, comprised sixty-seven and one-half percent by weight of the liquid material. On the basis of solids, the added two hundred and fifty grams of calcium hydroxide converted to calcium nitrate comprised fourteen and three-tenths percent by weight of the total solids of the reaction product. The hydroxides of other Group II metals forming water-soluble salts may be substituted for calcium hydroxide. In the case of guanidine sulfate, magnesium hydroxide is preferred.

Example II

Semi-bleached Kraft pulp was beaten to a Schopper-Reigler freeness of six hundred cc. in a laboratory beater at a consistency of two and four-tenths percent. To each of three portions of this pulp stock comprising two grams of dry fiber was added one and one-tenth cc. of a latex comprising forty percent by weight of an acrylonitrile-butadiene copolymer (fifty-five Mooney plasticity, forty percent acrylonitrile, sixty percent butadiene by weight, emulsified by means of fatty acid soap). The latex was thoroughly stirred with the pulp suspension and precipitation was brought about by addition of: *a.* One cc. of four percent solution in water of the reaction product of guanidine carbonate and formaldehyde. *b.* One-quarter cc. of four and four-tenths percent solution in water of the mixed precipitating agent described in Example I. *c.* One-half cc. of a water solution comprising three percent calcium chloride and three percent pentamethylene tetramine chloride.

In each case the precipitation of the dispersed polymer was complete with gentle mixing. Hand sheets molded from each of the above showed clear white water and physical tests on all the sheets were equivalent within limits of experimental error.

Example III

In a trial on a paper machine, Kraft pulp of two hundred and fifty cc. Canadian Standard Freeness was mixed at two percent consistency with sufficient latex (butadiene-acrylonitrile, sixty percent to forty percent by weight, Mooney viscosity one-hundred twenty-five, dispersed by means of five percent by weight of soap) to provide twenty-two and one-half percent by weight of copolymer of the weight of oven dry pulp. Precipitation of the dispersed polymer of the latex onto the pulp was accomplished by the addition, as ten percent solution in water, of an amount of solids equivalent to two and one-quarter percent by weight of the latex solids of the mixed precipitating agent described in Example I.

The paper machine was equipped with an open head box and a Bird screen. The pulp now comprising twenty-two and one-half per cent dry rubbery polymer precipitated onto or intimately mixed with the fibers was sent through a Jordan and made into paper of basis weight of seventy pounds per ream (480 sheets, 24″ x 36″). The pH of the paper machine system was six and seven-tenths to seven and four-tenths during the run. No foam was encountered.

Example IV

Paper (five hundred grams) from the run described in Example III was torn into small pieces and put into a laboratory paper beater with eighteen liters of cold tap water. After five minutes of circulation, three thousand five hundred grams of weights was placed on the bed plate of the beater, and operation continued. After fifteen minutes the paper was completely defibered. Hand sheets molded from the resulting stock were of excellent formation and showed physical test results nearly equal to that of the original paper.

Example V

Dispersions of the following fibers in water (two percent consistency) were treated as described in Example II with the same latex:

a. Asbestos
b. Rayon (acetate)
c. Glass
d. Groundwood
e. Sulfite

Precipitation required in all cases except (*a*) the same quantity of precipitating agent as in Example II. Sample (*a*) required only about sixty percent of that quantity.

Example VI

To fifty grams of free guanidine base dissolved in four-hundred-and-fifty cc. of water was added one hundred cc. of thirty-seven percent formaldehyde, and the resulting solution heated to boiling for thirty minutes. At the end of this time one drop of the resin solution added to four hundred cc. of water containing .02 gram of synthetic rubber in a colloidal dispersion caused immediate clouding. The remainder of the resulting solution was cooled and found to contain twenty-one percent solid resin. The pH (colorometric) of the solution at room temperature was nine and five-tenths. Two one-hundred cubic centimeter portions of the solution were taken out and treated as follows: A. Neutralized with concentrated acetic acid, phenophthalein end point. B. Neutralized with concentrated hydrochloric acid to phenophthalein end point and two grams of technical grade calcium chloride dissolved in the resulting solution.

Hand sheets were prepared as follows: Portions of semi-bleached Kraft pulp of seven hundred cc. Schopper-Riegler freeness comprising one gram of dry pulp were weighed out and diluted to three hundred cc. To each such portion of pulp was added one cc. of a synthetic rubber latex (seventy-five per cent acrylonitrile, twenty-five percent butadiene, Mooney viscosity about one-hundred-twenty-five, dispersed by means of soap), comprising thirty-nine percent rubber solids. The amount of precipitating agent, (A) and (B) above, and of untreated free guanidine-formaldehyde resin (called "C" below) required to yield clear white water when hand sheets were made from the treated pulp were:

A—0.2 cc.
B—0.02 cc.
C—0.4 cc.

All water soluble salts of Group II metals may be used in the practice of the invention as disclosed in this specification. Those of relatively high solubility are greatly preferred for convenience in handling and shipping the concentrated precipitating agent. However, at advantageous levels of pulp consistency when precipitation takes place any water soluble salt of a Group II metal is usable.

Among preferred salts are the soluble sulfates, nitrates, chlorides, bromides, iodides and/or acetates. Satisfactory results may be obtained with barium acetate, barium bromide, barium butyrate, barium chlorate, barium chloride, barium cyanide, barium dithionate, barium formate, barium hypophosphite, barium iodide, barium nitrate, barium perchlorate, barium permanganate, barium peroxydisulfate, barium propionate, barium tetrasulfide, barium thiocyanate, calcium acetate, calcium bromide, calcium chlorate, calcium chloride, calcium chromate, calcium dithionate, calcium formate, calcium hypophosphite, calcium iodide, calcium lactate, calcium nitrate, calcium nitrite, calcium perchlorate, calcium permanganate, calcium thiosulfate, magnesium acetate, magnesium chloride, magnesium citrate, magnesium chromate, magnesium formate, magnesium hypophosphite, magnesium iodate, magnesium iodide, magnesium nitrate, magnesium perchlorate, magnesium potassium chloride, magnesium sulphate, magnesium thiosulphate, strontium acetate, strontium bromide, strontium bromate, strontium chlo-

rate, strontium chloride, strontium dithionate, strontium ferrocyanide, strontium formate, strontium iodide, strontium lactate, strontium nitrate, strontium nitrite, strontium permanganate, and/or strontium thiosulfate. Any of these salts may be substituted in the foregoing examples for the salts shown. The salts may be added as hydroxides either as illustrated in Example I or by addition to the aqueous solution of reacted guanidine base.

Many other embodiments of the invention will occur readily to those skilled in the art and are included in its spirit.

The claims are:

1. The method of manufacturing internally bonded fibrous webs which comprises forming a dispersion containing fibers suitable for sheeting by conventional web forming procedures, particles of non-fibrous material capable of bonding said fibers upon deposition of said material on said fibers and the formation of a web thereof, and a composition effecting coagulation of said non-fibrous material on said fibers, said composition comprising a mixture of a poly-N-basic water soluble polymer and a water soluble salt of a bivalent metallic ion, and forming an internally bonded fibrous web of said fibers and bonding particles by sheeting the dispersion.

2. The product formed in accordance with the process of claim 1.

3. The method of manufacturing internally bonded fibrous webs which comprises forming a dispersion containing fibers suitable for sheeting by conventional web forming procedures, particles of non-fibrous material capable of bonding said fibers upon deposition of said material on said fibers and the formation of a web thereof, and a composition effecting coagulation of said non-fibrous material on said fibers, said composition comprising a mixture of a poly-N-basic water soluble polymer and a water soluble salt of a bivalent metallic ion, said mixture being formed by reacting a guanidine salt and formaldehyde in the presence of the hydroxide of a Group II metal adapted to form a water soluble salt with the ion of said guanidine salt, and forming an internally bonded fibrous web of said fibers and bonding particles by sheeting the dispersion.

4. A process in accordance with claim 1 wherein the metal ion is selected from the group consisting of calcium, barium, strontium and magnesium.

5. A process in accordance with claim 4 wherein the poly-N-basic compound is at least one reaction product of guanidine and aldehyde.

6. A process in accordance with claim 4 wherein the hydrogen ion concentration at the point of precipitation is at least about five and five-tenths and not more than about nine.

7. A process in accordance with claim 5 wherein the molar ratio between said reaction product and said salt is from about one-tenth of one mol of metal to about ten mols of metal per mol of reaction product.

8. A process in accordance with claim 5 wherein said metal ion is added as metal hydroxide.

9. A process in accordance with claim 5 wherein said reaction product is added as a salt.

10. A process in accordance with claim 5 wherein the reaction product comprises a reaction product of guanidine and formaldehyde.

11. A process in accordance with claim 10 wherein the molar ratio between metal ion and reaction product is from about two-tenths of one mol of metal ion to about seven-tenths of one mol per mol of guanidine aldehyde reaction product.

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