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2,807,543

**METHOD OF PREPARING FIBER DISPERSIONS
CONTAINING AN ELASTOMERIC BINDER**

Raymond C. McQuiston, West Newton, Mass.

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This invention relates to improved fiber dispersions, more particularly to a novel method of depositing beneficially functioning colloidal material on fibers to produce fiber-base products of marked utility.

This application relates to improvements on the type of process described in the copending application of R. C. McQuiston et al., Serial No. 720,480 filed June 6, 1947 now Patent 2,666,699.

A major object of the invention is to establish an aqueous system in which fibrous materials and colloidal substances such as latices of elastomeric material are dispersed and to adjust and control the electrochemical character of the system to insure a gradual and complete adsorption of the colloidal material on the surfaces of the fibers.

Another object of the invention is to provide a method in which colloiddally dispersed materials can be deposited on a fibrous base in peptized or uncoagulated or unagglomerated form.

The present invention provides a method of producing aqueous fibro-colloidal dispersions which is free-running and may be readily sheeted and dewatered with substantially no loss of the colloidal binder material in the white water to produce highly coherent sheet material of excellent physical characteristics. The improved aqueous fiber-colloidal dispersion may be sheeted in conventional paper-making machines.

The method of the invention insures a broad choice of specifically different fibers and colloidal binder material to produce ultimate sheet stock of varying and selected physical characteristics. A particular feature of the invention is that it permits the use of natural or synthetic rubber latex in very high proportions to produce tough, pliable, rubbery sheet materials. The products producible by the method of the invention comprise pliable unified papers which are fine grained and homogeneous and which are characterized by a strikingly high density, toughness and resiliency and further display very high wet strength and resistance to various solvents, depending on the nature of the particular colloidal binder employed.

The characterizing feature of the invention, i. e., the adsorption of the colloidal binder in peptized or truly colloidal form on the surfaces of the fiber base, insures a firm bond in which the fibers are so bonded and held that the ultimate sheeted stock cannot be delaminated or split. The sheeted stock or papers produced according to the invention have a wide field of use and, depending on the formulation of the fiber-colloid dispersion, may be employed as backings for pressure-sensitive tapes, backings for waterproof abrasive sheets, such as sandpaper, gasket sheeting, artificial leather package and container sheeting and the like. The finished sheets can be coated with suitable surface coating compositions either during the production of the paper or at any subsequent time.

A very valuable feature of the invention is that it permits the addition of suspensions of finely divided, non-colloidal particles in the aqueous dispersion without dis-

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turbing the electrochemical balance of the system and the true colloidal deposition of the binder on the fibers. This can be achieved by proper peptization of the non-colloidal suspensoid (such as zinc oxide and other pigments and fillers, sulfur vulcanizing agents etc.) so that it does not adversely affect the dispersed colloid binder phase either prior to or during deposition and adsorption of the binder on the fibers.

As was explained in the prior application referred to, gradual deposition of colloidal binder material upon fibers may be achieved by carefully controlled conjoint use of a soluble aluminum salt such as aluminum sulfate and a soluble chromic salt with the proper adjustment of the pH values during the procedure. While such a method is effective, it does present certain disadvantages, particularly because of the necessity of controlling the balance between the aluminum salt and the chromic salt. Extensive study and research clearly establishes the undesired effect of the aluminum salts in a system of the present type wherein the desideratum is the gradual deposition of colloidal material in truly colloidal sizes on the surfaces of fibers. The aluminum salts and other similar strongly hydrolyzable coagulants tend to effect a rapid precipitation of the sensitive elastomeric colloids. This is due to the action of the strong coagulant in neutralizing the change on colloid before its deposition on the fiber. This results in the reduced retention of the colloid binder on the fiber with concomitant increased cost of operation and poorer quality of the finished products.

As explained in the earlier application, the major problem in a system of the type herein described is to insure the gradual adsorption of colloidal binder particles upon the fiber surfaces with the result that the initial system comprising a mixed aqueous dispersion of fibers and colloidal binder particles is converted or transformed into a system in which the fibers are coated with adsorbed binder particles of true colloidal dimensions which coated fibers remain in stable dispersion in the aqueous phase. To insure the desired results this transformation must be achieved without causing coagulation of the colloidal system resulting in large curds or lumps of particles (which may include fibers) which are not deposited and adsorbed on the free fibers and which cannot be redispersed because of the irreversible nature of the colloid system. This complex colloidal system is very delicate and very sensitive to adverse influences. A complicating factor is that the very agents which are effective in producing deposition of the colloidal particles on the fibers are also capable of causing coagulation. Thus the problem cannot be solved merely by the use of coagulating agents. The problem is aggravated when it is attempted to use large proportions of irreversibly coagulative colloidal particles and to substantially entirely deposit them upon the fibers.

In such a colloid-fiber aqueous dispersion the fibers and colloidal particles are each negatively charged and normally repel each other. The invention, in effect, provides a simple method of introducing electropositive particles into the system which are selectively attracted to the surfaces of the fibers which in turn attract and bind or hold the negatively charged colloidal binder particles. If the positively charged particles should prematurely neutralize or discharge the negatively charged dispersed binder particles, the latter would coagulate or agglomerate without being properly deposited on the fiber.

The present invention avoids the objections inherent in the use of aluminum salts during the process of depositing the colloidal binder on the fibers. In the novel procedure a chromic salt is employed alone in a properly alkalized aqueous fiber-colloid dispersion to insure the gradual migration of the colloid material to and deposition upon the fiber in its peptized state.

The invention stems from the concept of utilizing the special characteristics of chromic salts under controlled conditions of pH to achieve the gradual deposition of the colloidal binder particles on the dispersed fibers. This is achieved, as will be seen, by insuring a slow solvation of a chrome-salt from an inactive to a soluble form. When a hydrolyzable chromic salt, such as chromic sulfate, is dissolved in water and the pH adjusted to about 6.2 or above, the salt is converted to the insoluble inactive chromic hydroxide. In this inactive form the chrome will not precipitate latex. This characteristic of hydrolyzable chromic salts such as the sulfate and nitrate is invoked to secure the desired gradual and complete deposition of the colloidal binder particles on the fiber. As will be seen, improved results are achieved under the invention by employing a special alkalizing agent in the process.

Considered briefly, the invention comprises forming a dispersion of a selected fiber or fibers in a beater, adjusting the pH to a range of pH 8.8 to 10 depending on the extraneous salts in the water. Preferably this adjustment is done with ammonia or other suitable organic or inorganic ammonium compounds with or without supplementation with chelating, complexing or sequestering agents which are effective under alkaline conditions. Such agents may include sodium meta phosphate, tetra sodium polyphosphate, polyoxyethylene, lauryl alcohol, "Versene" (sodium salt of ethylene diamine acetic acid), and the like.

In the preferred operation "Tamol" (a neutral sodium salt of a condensation product of formaldehyde and crysilic acid which is sulfonated and saponified) is added to the dispersion. This functions beneficially in the process, particularly in acting as a protectant or retardant. In lieu of Tamol, an ammonium salt of an equivalent condensation product may be employed.

Thereafter a rubber latex or similar elastomer dispersion is introduced. When the formed sheet is to be subsequently vulcanized, vulcanizing agents may be introduced at this stage. When dyes and pigments are employed, it is preferable to add these prior to the addition of the latex.

It is to be observed, at this point, that one of the marked advantages of employing ammonia for the alkalizing agent is that it insures the homogeneous dispersion of the latex and permits the introduction of the latex into the furnish without the necessity of employing protective colloid as it has a peptizing action on the rubber colloids. The poly phosphate functions similarly, i. e., it tends to prevent agglomeration or precipitation and especially in conjunction with ammonia acts to prevent the build-up or aggregation of rubber particles above colloidal size. The use of ammonia thus insures a clean running stock with no sticking on the paper-making equipment.

Thereafter, a suitable hydrolyzable chromic salt, such as chromic sulfate, is added preferably in predissolved form and the beater is circulated until the deposition of the colloidal binder on the fibers is complete. The chromic salt is added in an amount sufficient to adjust to a pH of between 5.1 and 5.6 depending on the fibers employed and the additives in the furnish. For example, if zinc oxide is added to the fibro-colloidal dispersion, it functions as an alkali and hence more of the chrome salt is required.

When deposition is complete, it is necessary to maintain the dispersion at a pH of between about 4.2 and 5.2 through the chest and paper machine. This may be done with any suitable acid or soluble acid salt. For this purpose, it is preferred to employ aluminum sulfate because of its complexing action with the chrome. The amount of alum which is added depends on the colloids and fibers employed. For example, furnishes which contain sulfate, hemp and bast fibers require a greater percentage of the aluminum hydrate than does bleached

sulfite. The aluminum hydrate has a salutary effect on the pectin of bast fibers. It also has a beneficial effect on rags because of the more porous or permeable character of this stock requiring more surface coverage.

It is particularly to be noted that the aluminum sulfate is added to the slurry only after the deposition of the elastomer colloid is complete. It is employed essentially as a regulator of acidity at the end of the fibro-colloid adsorption and for its mechanical effect in providing a free stock. The aluminum hydrate which is formed precipitates on the fibers and is advantageous.

The process can be supplemented, when desired, with any suitable tub sizing operation. The invention can be more readily comprehended and evaluated from a consideration of a typical and illustrative procedure for preparing beater stocks, for subsequent formation into highly uniform, tough, dense sheets of a high rubber content.

A beater may be loaded with the required amount of water and then charged with 800 pounds (dry weight basis) bleached sulfates.

The fibers are then beaten for the time necessary to achieve the desired dispersion of the fibers. This period may vary depending on the stock used and may be of the order of eight hours more or less. After the desired dispersion of fibers has been achieved, the pH of the slurry is adjusted to pH 8.8 to 9.2 with aqueous ammonia in an amount of about 5 to 6 lbs. of ammonia depending on the condition of the water used in the beater. There is then introduced 3.5 lbs. of sodium triphosphate and about 10 lbs. of aniline base dyestuff. When dyestuff is not incorporated 3.5 lbs. of Tamol is added to the circulating slurry. Rubber latex is then introduced in an amount which is required to impart the selected physical characteristics. In a typical case 900 lbs. of synthetic (GRS) rubber latex (38% solids) is added. At this stage from 3.5 lbs. to 4.5 lbs. of an anti-oxidant is introduced in the form of a solution containing, if desired, casein or other peptizing agents previously ball milled to form a dispersion. At this stage also vulcanizing agents may be added. This, for example, may comprise 3.5 to 4.5 lbs. of sulfur and butyl zymate which is added to the circulating pulp as a 50% aqueous dispersion. At this point also selected rubber plasticizers, latices of resin elastomers and the like may be added.

Thereafter a chromic salt such as chromic sulfate is introduced into the colloid-fiber aqueous dispersion. This preferably is added in about 120-140 lbs. of a 25% solution (30-35 lbs. solids). The beater is continued in circulation until deposition is complete which, in the usual case, requires from about 15 to 30 minutes. After the deposition of the colloidal material on the fibers, aluminum sulfate is slowly added to the circulating stock. This, preferably, is added in predissolved form in an amount of from 10 to 15 lbs. of solid aluminum sulfate which adjusts the slurry to pH 4.2 to 5.2.

The resulting dispersion is eminently stable but is improved for most paper making purposes by several days of aging. Microscopic examination of the dispersion discloses the deposition of minute colloidal latex particles upon the outer surfaces of the cellulose fibers with substantially no agglomeration into lumps or aggregates of rubber.

This beater slurry may be formed into papers of various ream weights on conventional paper-making machinery such as the regular "cylinder machine."

In this operation the slurry is pumped from the beater to the chest with addition of water to establish the desired transfer consistency and then transferred to the machine chest. Prior to running on the paper machine, the slurry is diluted with water in a mixing box so that the slurry arriving at the wet end of the machine is reduced to paper-making consistency of about 0.5% by weight of coated fibers.

It is found that with such a procedure there is excellent

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bonding of the colloidal rubber particles to the fibers and substantially no loss of rubber in the white water.

The sheeted stock dries readily on the dryer cylinders in a period of about 5 minutes at a temperature of about 220° F. thus effecting vulcanization of the rubber phase. The dried paper may be subjected to any form of cold calendering.

It will be understood that the preceeding typical example is illustrative of the general procedure. As noted perviously, the products produced from this process may vary in character and physical properties depending on the fibers employed and the character of the elastomer latex utilized, and the type of adjuvants used. The fibers employed may comprise cellulosic or vegetable fibers, leather, wool fibers, asbestos, either along or in predetermined admixture. Thermoplastic and thermo-setting resinous material may be utilized in the process either alone or in combination with dispersed rubbers. The fibro-colloidal dispersions of the invention may be employed in producing relatively thick setting materials such as floor coverings and the like, stiff leather-like sheets for shoe inner soles and mid soles, for the manufacture of luggage and the like. There is thus a wide permissive field for the products of the invention whose utility is extended and enhanced by the novel characteristics of the dispersion.

While a preferred mode of procedure has been described, it is to be understood that this is given didactically to illustrate the underlying principles of the process and particularly the novel concepts of the utilization of hydrolyzable chrome salts under the specified conditions to insure a gradual and peptized deposition of elastomer colloids on the surfaces of fibers. The improvements of the invention also include the correlated use of ammoniated rubber and fiber-containing slurries with chromic salts for the production of new and improved fibro-colloidal dispersions.

I claim:

1. A method of making aqueous fibro-colloidal dispersions comprising forming a dispersion of fibers in water substantially free from aluminum salts alkalized to a pH value of between 8.8 and 10; admixing a dispersion of colloidal elastometric binder particles to form a mixed dispersion; adding a chromic salt in an amount sufficient to reduce the pH of the system to between 5 and 5.6, to effect a gradual peptized deposition of the dispersed colloids on the fiber and then adding an acidifying agent to reduce the pH to between 4.2 and 5.2.

2. A method according to claim 1 in which chromic sulfate is the chromic salt.

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3. A method according to claim 1 in which the fibers are cellulosic fibers and the colloid binder particles are rubber latex.

4. A method according to claim 1 in which the water is alkalized with an ammonium compound.

5. A method in accordance with claim 1 in which the water is alkalized with ammonia.

6. A method according to claim 1 in which the fibers are cellulosic fibers, the colloidal binder particles are rubber latex and the water is alkalized with ammonia.

7. A method according to claim 1 in which a vulcanizing agent is incorporated in the system prior to the addition of the chromic salt.

8. A method according to claim 1 in which the acidifying agent is aluminum sulfate.

9. A method according to claim 1 in which the water is alkalized with ammonia, the fibers are cellulosic fibers, the colloid binder is rubber latex and the acidifying agent is aluminum sulfate.

10. A method according to claim 1 in which sequestering and chelating agents are incorporated in the dispersion prior to the addition of the chromic salt.

11. A method according to claim 1 in which the acidifying agent is a mineral acid.

12. A method of preparing an aqueous fibro-colloidal slurry adapted for use in making unified sheet material on paper-making machines comprising dispersing paper-making fibers in water free of aluminum salts, to form a fibrous slurry, alkalizing the slurry to a pH of 8.8-10 with an alkaline agent, admixing a colloidal binder polymer latex, introducing a quantity of chromic salt sufficient to reduce the pH to 5-5.6 to insure the gradual peptized absorption of latex on the fibers and subsequently adjusting the slurry to a pH of between 4.2-5.2 with an acidifying agent.

13. A process in accordance with claim 12 in which the paper-making fibers are cellulosic fibers.

14. A process in accordance with claim 12 in which the alkaline agent is aqueous ammonia.

15. A process in accordance with claim 12 in which the acidifying agent is aluminum sulfate.

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