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PRECIPITATING SIZE WITH CHROMIUM
AND ALUMINUM SALTS

Raymond C. McQuiston, West Newton, and Frank E. Davenport, Newton Center, Mass., assignors to Minnesota Mining & Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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This invention relates to aqueous fibro-colloidal dispersions, methods of preparation, and products made therefrom.

An object of the invention is to produce stable dispersions of fibers wherein each fiber has an adsorbed coating of colloidal binder particles which have been deposited from an initial colloidal dispersion thereof by a procedure involving a correlated utilization of aluminum and chromic salts coupled with a shifting and control of pH values.

Such dispersions are to be distinguished from mixed dispersions such as result when a dispersion of fibers is mixed with a dispersion of colloidal particles but without the latter becoming bound to the surfaces of the former.

The invention provides aqueous fibro-colloidal dispersions which are adapted to be sheeted and dewatered with little or no loss of the colloidal binder material in the white water (i. e. in the water which is separated from the coated fibers), to provide highly coherent finished sheet materials of excellent strength and toughness, including papers of various types. The sheeting may be formed on paper-making machines.

A great variety of fibers and of colloidal binder materials may be utilized to produce sheet materials having different properties adapted for many different uses. Use may be made of rubber latex (natural or synthetic) to produce tough, rubbery sheet materials; and a feature of the invention is that high proportions of such rubber may be incorporated.

An object is to provide stable dispersions of paper-making fibers in which the fibers are coated with latex particles of natural or synthetic rubber (elastomer polymers), or plastic polymers. Such latex particles have a highly coagulative propensity, and a feature of the present invention is the ability to handle such materials. These dispersions may be prepared in large scale batches in a beater and then processed on commercial paper-making equipment to produce novel types of paper. Use can be made of cylinder machines, Fourdrinier machines, and wet machines. In this connection it is emphasized that laboratory experiment procedures quite commonly fail to work out satisfactorily when transferred to the paper mill. The present invention provides procedures which are adapted for use in regular full-scale commercial operations.

An object is to produce pliable unified papers containing high proportions of natural or synthetic rubber (30-150% or more), which are fine-

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grained and highly uniform and homogeneous; which have a remarkable density, toughness and resiliency; which have a high wet-strength and which are impermeable to various solvent materials (depending on the nature of the particular rubber employed); and in which the fibers are so firmly held and unified that the paper cannot be split or delaminated nor the fibers be pulled loose at the surfaces. Creped papers can be made by creping the paper stock prior to completion of the normal paper-making operation, while still in a moist condition. An object is to produce unified papers which can be employed as the backings for pressure-sensitive adhesive tapes (such as masking tapes, shoe tapes and electrical tapes), backings for waterproof abrasive sheets in the nature of sandpaper, and as gasket sheeting, package and container sheeting, artificial leather, etc., making possible products having novel and valuable properties not heretofore obtainable. The paper can be coated during the making procedure by applying a coating composition at a calender stack.

The invention has a wide field of application in making possible the production of a great variety of sheeted products, as it is not limited to vegetable fibers nor to the making of paper. Mineral and animal fibers can be used. Asbestos fibers, cork fibers, wool fibers and leather fibers, for example, can be used, either alone or in admixture with the common cellulose paper-making fibers. The colloidal binder material is not limited to substances of any particular chemical composition. Thermoplastic and thermosetting resin materials can be used, alone or in combination with rubbers. Proteins (such as casein and glue) can be used. Colloidal coloring agents can be included. The dispersions of this invention may be employed in making relatively thick sheetings, such as floor coverings, and stiff leather-like sheets useful for shoe midsoles and inner soles and in making luggage, etc. Dispersions may also be made for use as coating compositions and cements.

A feature of the present invention is that the technique permits of including a suspension of finely divided non-colloidal particles in the aqueous dispersion (as illustrated by zinc oxide and other pigments and fillers, and by sulphur vulcanizing agents, for example). Proper peptization of the non-colloidal suspensoid is maintained so that it does not adversely affect the dispersed state of the colloidal particles prior to deposition nor the deposition thereof on the fibers. Such suspensoid is retained and carried

into the final dewatered sheet as a uniform mix distributed throughout the fibro-colloidal phase. A tub-sizing procedure can be used for incorporating impregnants into the sheet during the making operation.

The character of the final sheet can be modified by heating and by subjecting to the action of solvents, with or without pressing or calendering, depending upon the nature of the binder material employed.

The present invention is based upon our discovery of the controlled deposition effects which can be produced by a properly correlated conjoint use of a soluble aluminum salt (such as aluminum sulphate), and a soluble chromic salt (such as chromic sulphate), when coupled with a properly controlled shifting of pH values. Other examples of such aluminum and chromic salts are aluminum chloride, aluminum nitrate, basic chromic sulphate, chromic chloride, and chromic nitrate. These are all trivalent salts of strong acids. The chromic salts have the so-called co-ordination type of structure.

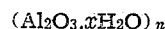
The problem is to cause the dispersed binder particles to be gradually adsorbed upon the fiber surfaces; so that a system of mixed colloidal particles and fibers, dispersed in water, is transformed into a system in which the fibers are coated with adsorbed binder particles while remaining stably dispersed in the water. The great difficulty is that this transformation must be accomplished without causing a coagulative collapse of the system resulting in large curds or lumps of particles (which may include fibers), which are not deposited on the free fibers and cannot be redispersed due to the irreversible nature of the colloidal system. This complex electro-colloidal system is delicate and extremely sensitive to adverse influences, and it is unfortunately true that the very agents which are effective in producing deposition of the colloidal particles upon the fibers are also capable of causing coagulation. Hence the problem cannot be solved by the mere use of coagulating agents. The problem is especially acute when it is attempted to use large proportions of irreversibly coagulative colloidal binder particles and to substantially entirely deposit them upon the fibers.

The fibers and the colloidal binder particles each are electro-negatively charged in a mixed dispersion in water, and hence normally repel each other. The present invention provides a way of introducing electro-positive particles into the system which are selectively attracted to the surfaces of the fibers and in turn attract and hold the negatively charged colloidal binder particles. Thus the binder particles become coated upon and bound to the fibers by what may be termed an "electrostatic cement." A difficulty which had to be overcome was that if the positively charged "electrostatic cement" particles should prematurely discharge the negatively charged dispersed binder particles, then the latter would coagulate or agglomerate without being deposited properly upon the fibers.

The aluminum and chromium salts which we employ are individually capable of producing strong positive ions or particles in aqueous solutions, which have a pronounced precipitating action on dispersed colloids. But neither one alone produces the desired results, especially under the conditions necessarily encountered when working with large batches and with highly coagulative colloids, in respect to the fibro-colloidal type of system with which we are concerned. The con-

joint use which we make of these two types of compounds does not involve a mere additive or complementary action, since there is an interaction whereby the effect of each is modified or altered. By way of background to an understanding of our invention, it is desirable to point out the following facts concerning these compounds.

The aluminum salt (such as aluminum sulphate) produces various hydrolytic and ionic products when put into water, depending on the acid-alkaline condition prevailing. (This condition is most conveniently expressed in terms of the pH value of the solution. The pH scale goes from 0 to 14, with a pH of 7 indicating a neutral condition, lower values an increasingly acid condition, and higher values an increasingly alkaline condition.) At pH values of 4.0 to 6.0, aluminum sulphate (for example) interacts with water to produce positively charged hydrated alumina particles having the formula:



which can be adsorbed on the negatively-charged fibers to act as an "electrostatic cement" for precipitating and retaining the colloidal binder particles. Increase of the pH value leads to a different type of charged alumina which is not effective for the desired cementing action. Further increase of the pH value to above 10.0, results in the alumina becoming largely converted to a negatively charged aluminate. When the pH value is depressed below 4.0, less of the desirable "electrostatic cement" alumina is available, as it reverts to aluminum sulphate which is ionized to form positive aluminum ions (Al^{+++}) instead of hydrolyzing to form the positive alumina particles. The pH value which exists depends in part on the concentration of aluminum sulphate which is introduced into the water, since it is an acidic material, and in part on whatever other substances are introduced which exert an acidifying or alkalinizing action. Thus sulphuric acid can be used for acidifying and sodium hydroxide for alkalinizing.

The aluminum salt is most effective in providing an "electrostatic cement" action when the pH value is within the range of 4.0 to 6.0; the optimum pH value being approximately 4.8 to 5.2, at which the strongest electropositive potentials are produced.

When the readily coagulative colloids, such as rubber latex, are present it is difficult to avoid sudden coagulation thereof when positive ions or particles are introduced. This is especially true when working with large batches, due to the substantial time factor involved before introduced substances can become uniformly distributed by mixing so as to have the intended concentration, and due to other effects. Hence the difficulty of merely using the aluminum salt in attempting to produce the results aimed at by us, owing to its strong propensity to cause coagulation and to cause rapid deposition.

The water-soluble chromium co-ordination salts, such as chromic sulphate, provide charged chromium nuclei having valuable properties in the present connection. In accordance with Werner's theory, the positive chromium ion of each molecule is surrounded by six co-ordinative groups, the whole constituting an ionic nucleus having an electrostatic charge, outside of which are located the remaining radicals or ions of the molecule, which are oppositely charged and held by the primary electrostatic valence forces. In aqueous solution, the aforesaid chromium

nucleus constitutes a large charged ion, consisting of the central chromium ion surrounded by its 6-co-ordinative groups, which may be H_2O or anion groups. A given nucleus can be altered by penetration of one or more anions which displace the H_2O or anion groups previously present, and in this way the charge of an electropositive nucleus can be reduced and it can even be made electronegative. The penetrating ion may be either an outer ion of the chromium compound itself, or may be supplied by some other compound present in the solution. The modification of the charged chromium nucleus, and its consequential modification of its environment, are caused or influenced by various conditions, including the acidity or alkalinity of the solution, etc.

An enlarged chain type of charged chromium nucleus can be produced by penetration of hydroxyl ions which link together adjoining chromium ions (a process called olification). The chromium sulphates lend themselves particularly to the formation of positively charged, stable, complex chain structures, which have the greatest electropositive potential within the pH range of 4.8 to 5.2. At pH values below 4.8, sulphate ions can penetrate the nucleus and displace H_2O groups, and this can even be carried to the point of producing a negative nuclear ion.

The chromic salt is most effective in providing an "electrostatic cement" action when the pH value is within the range of 4.0 to 6.0, the optimum pH value being approximately 4.8 to 5.2.

Thus it is evident that the presence of charged chromium nuclei can profoundly influence the ionic and electric properties of a solution, the functioning of other compounds present, and the state of fibro-colloidal dispersions therein, and that the effect is a function of the pH value and of other substances present. That is why, in regard to the present invention, it has been stated that the aluminum and chromic deposition salts act in a conjoint fashion which is not merely additive or complementary. The positively charged chromium nuclei per se can act as a so-called "electrostatic cement," but conjoint use with the aluminum salt is necessary to produce the results we desire.

A method of making stable fibro-colloidal dispersions, in accordance with this invention, will now be described in a step-by-step manner which includes a discussion of the principles involved; to be followed by the detailed description of illustrative examples. It is obviously impossible to set forth specific detailed directions for all possible fibro-colloidal systems; but it is possible to analyze the basic procedure and indicate the governing principles so that those skilled in the art will be able to practice the invention generally, making whatever adjustments are necessitated by any particular situation.

First stage

The fiber material is dispersed in water to form a fibrous slurry. In making paper, this is represented by the beating of the cellulose paper-making fibers, which produces dissemination of the fibers, and a substantial reduction in dimension may occur. The dimension and kind of the fibers, and the degree of hydration (if any), influence their properties for adsorption of the binder particles. Hydration is not required.

Second stage

The dispersed fibers are preferably conditioned

by adding a small proportion of the chromic salt to provide electropositive chromium nuclei, and preferably also a small proportion of the aluminum salt, especially when a paper-making stock is being prepared. These may be added in dry form or in solution form. Thus equal parts by weight of chromic sulphate and aluminum sulphate may be added, in amount which produces an acid pH value in the range of approximately 4.0 to 6.0. The aluminum salt may be omitted, but in such case the final "white water" may not be so clear. The result of this stage is to cause adsorption of positive particles (serving as an "electrostatic cement") on the fiber surfaces so that they will be preconditioned to a certain extent before the binder colloid is introduced. However, this is done to a limited extent only, to avoid undue flocculation or agglomeration of the binder colloid when introduced. This stage is an optional one and is not needed when the subsequent stages are performed in substantially optimum fashion.

Third stage

An alkalizing agent is added, such as sodium or potassium hydroxide, or sodium or potassium silicate, for the purpose of shifting the pH value to a strongly alkaline value which will inactivate the coagulative propensity of the aluminum and chromium deposition agents employed in the process. The pH value should be raised to above 10.0 and preferably to 10.5-11.0 or higher. When an alkali-metal silicate is used in whole or in part as the alkalizing agent, colloidal hydrated silica may be formed and, in any event, the deposited binder colloid will contain adsorbed silica which will thus be incorporated in the final dewatered sheet. Its presence in the sheet will impart desirable properties for certain purposes, such as increased resistance to penetration by organophilic oils and solvents, especially when the proportion (SiO_2 basis) is at least 5% by weight of the fibers. A complex of fiber-adsorbed latex particles and silica has novel properties as compared to the properties resulting when the silica is omitted. When a strong alkali, such as sodium hydroxide is used, it may be replaced in part by an alkaline buffer salt of a strong base and a weak acid, such as di-sodium phosphate.

Fourth stage

A dispersion of the binder colloid is added and thoroughly distributed. For example, this may be in the form of a latex of natural or synthetic rubber, containing a mildly alkaline stabilizing agent. Thus the synthetic rubber latex as obtained from the producing plant, may contain a soap; and natural rubber latex may contain ammonia. The proportion employed depends upon the kind of sheeting or coating ultimately desired. The present invention permits of incorporating extremely large amounts, for example the binder solids may exceed 100% of the fiber solids. The method permits of admixing a suspension of non-colloidal particles without adverse results. For example, a suspension of zinc oxide can be introduced as a filler or pigment. Vulcanizing agents can be introduced when a vulcanizable binder is used, so as to be present if the ultimate sheet is to be vulcanized.

A protein protective colloid is preferably incorporated to prevent the formation of small curds and to impart smoothness to the fibrous slurry, especially when large proportions of coagulative binder colloid are introduced. A type

which forms slowly and finely divided precipitable systems is best adapted to the present method. The gamma form of soybean protein (such as "Prosein") has been found to be highly suitable. Casein can be used. Only a small proportion is needed. This is introduced as an alkaline dispersion in water, and is added directly to the fibrous slurry, preferably after the binder colloid has been admixed.

Fifth stage

A small additional proportion of the chromic salt (such as chromic sulphate) is added to the slurry, which is thoroughly mixed. It functions in part as an adsorption retardant for the aluminum sulphate which, if added directly, would cause immediate, rapid precipitation or flocculation of the binder colloid. The amount needed thus depends on the amount of aluminum sulphate employed. The amount of salts thus far introduced is insufficient to cause deposition of the colloidal binder particles. The fibro-colloidal slurry has now been conditioned for the final step of depositing the colloidal binder particles on the fibers.

Sixth stage

The aluminum salt (such as aluminum sulphate) is added to the alkaline slurry in sufficient amount to cause the deposition of the binder colloid upon the fibers. The greater the amount of the binder colloid, the greater the amount of "electrostatic cement" needed to attract and bond the colloidal particles to the fibers. The pH is adjusted to an acid value within the range of 4.0-6.0. The optimum value is approximately 4.8 to 5.2. The aluminum salt also serves for adjusting the pH value due to its acidifying nature. The acidifying effect depends upon the concentration of the aluminum salt, which involves the amount of the aluminum salt relative to the amount of water present. An acid (such as sulphuric acid) can be added to produce the desired pH value if the amount of the aluminum salt employed is insufficient. If the desired amount of the salt results in too low a pH value, an alkalinizing agent can be added to raise the pH to the desired value. Because of the previous steps in the process, including the incorporation of the chromium nuclei in the preceding stage, this introduction of the aluminum salt results in an excellent deposition of the colloidal binder particles upon the fibers in a controlled manner which avoids coagulation and substantial formation of undeposited lumps or floccules. The resultant fibro-colloidal dispersion is stable and smooth and is adapted for forming dewatered sheets having the advantageous characteristics previously mentioned, with little or no loss of binder colloid material in the white water.

If the dispersion is diluted with water (which tends to raise the pH value), an acidifying agent should preferably be added to hold the pH value in the desired range, so as to prevent the colloidal binder particles from sluffing off from the fibers.

Aqueous dispersions of positively-charged binder and peptizing colloids may be added to the fibro-colloidal dispersion; for example, dispersions of melamine hydrochloride, urea resins, etc.

In the case of leather fibers which are either initially in the form of chrome leather or are chromium-collagenated in situ in the dispersion, it is necessary to employ an excess of the chromic salt so as to provide free inorganic chromium nuclei for the purposes herein required. In the case of vegetable-tanned leather fibers, a much

larger proportion of chromic salt is required than in the case of cellulose fibers (or even in the case of chrome-tanned leather fibers) as such vegetable-tanned leather fibers are very strongly charged negatively and tannic acid is present which adversely effects the desired result. In this case it is necessary to cause chromium ions to combine with carboxyl groups of the proteolytic fiber to enable a deposition of positive charges or particles on the surfaces of said fibers by means of the inorganic chromium nuclei. This process consumes a part of the total of the chromic salt, and hence a greater amount is needed in order to furnish the necessary free chromium nuclei.

If animal glue is used as the binder colloid, alone or in combination with another binder colloid, it is desirable to employ tannic acid and sodium chloride to produce precipitation of the glue as a glue tannate (glycine tannate), which provides negatively charged particles capable of effective deposition on the fibers by means of the chromium and aluminum compounds.

The following examples set forth procedures which we have successfully used in a paper mill for preparing beater stocks subsequently formed into highly unified and uniform papers or sheets having a high content of synthetic rubber. The descriptions of the beater treatment procedure are divided into six parts corresponding to the six stages previously discussed.

Example 1

(1) The beater was loaded with the required amount of water and was then charged with 800 lbs. (dry weight basis) of a semi-bleached kraft paper-making pulp (a sulphate type of pulp). Water was again added and the pulp was given a hard beating for eight hours, resulting in a pulp slurry containing about 3% of fiber pulp (dry weight basis). The pH value was 7.80. This pH value is subject to variation dependent on the pulp and on the pH value of the water used.

(2) There was then added 24 lbs. of commercial chromic sulphate and 24 lbs. of commercial aluminum sulphate (known as "paper makers' alum"). The weights given are for the commercial salts, which are hydrates. The chromic sulphate has the formula: $\text{Cr}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, and is a hydrated mixture containing about 27% H_2O by weight. The aluminum sulphate has the formula: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The salts were predissolved in small portions of water and added as 25% solutions to the slurry, and thoroughly mixed in for about 20 minutes. The resultant pH value was 4.10.

(3) There was next mixed in 270 lbs. of a 38% by weight solution of sodium silicate having an SiO_2 to Na_2O ratio of 3.25. The sodium silicate solids amounted to 12.8% of the cellulose paper stock (dry weight basis), thus providing 9.6% of SiO_2 relative to the paper fibers. Mixing was continued for about 20 minutes, and the resultant pH value was 10.10.

(4) The synthetic rubber latex was then introduced and thoroughly mixed for about 20 minutes. This consisted of 1,450 lbs. of "GRS No. 3," produced according to U. S. Government specifications in a Rubber Reserve Corporation plant. This rubber is a co-polymer of 50% butadiene and 50% styrene (commonly known as Buna-S type rubber). This latex contains about 2% rosin soap as a dispersant. The latex contains 38% rubber solids, which amount to 68.9% of the cellulose paper stock.

There was next mixed in 87 lbs. (dry weight) of a vulcanizing agent composition, known as

"G-3" (sold by R. T. Vanderbilt Co., Inc., of New York city), containing sulphur, butyl zimate as an accelerator, zinc oxide as an activator, hydroquinone mono-benzyl-ether as an antioxidant, and a small amount of casein and alkali as dispersants, which composition is ground in water to form a dispersion having a solids content of 52%. This vulcanizing composition can be omitted if it is not desired to vulcanize the synthetic rubber in the ultimate paper.

There was next mixed in a dispersion of gamma soybean protein. Use was made of "Prosein" (sold by the Glidden Company). The dispersion consisted of 15 lbs. of Prosein, 75 lbs. of water, and $\frac{3}{4}$ lb. of caustic soda. This provided protein in the proportion of 1.9% of the cellulose paper stock. About 20 minutes of mixing was employed to insure that the batch was thoroughly mixed before the next step.

The resultant pH value was 10.20

(5) There was next mixed in 24 lbs. of chromic sulphate, predissolved in water to form a 25% solution. The slurry was thoroughly stirred for about 20 minutes. The resultant pH value was 9.60 and the slurry was ready for the final introduction of aluminum sulphate to deposit the rubber particles of the latex upon the cellulose fibres.

(6) There was then slowly added 140 lbs. of aluminum sulphate, predissolved in water as a 25% solution, over a period of about 20 minutes, with mixing. The resultant pH value was 4.20. The slurry was further mixed and the colloidal rubber particles gradually deposited on the fibres, until deposition was completed and the white water was clear, requiring about 15 minutes.

The resultant dispersion was stable, and it was found that it was in better condition for paper making after aging for four or five days than it was initially.

Microscopic examination of the dispersion made clearly visible the deposition of the latex particles upon the outer surfaces of the tubular cellulose fibers and showed that but little had agglomerated to form separate clumps or bundles of rubber. These latter had a size no greater than the order of magnitude of the fiber diameters, but were sufficiently large so that they would be mechanically retained in the fibrous sheet formed in paper making, rather than passing off in the white water.

The total proportions of the chief ingredients can be summarized as follows, being expressed in percentage by weight relative to the cellulose paper fibers:

Kraft pulp (dry basis) -----	100.0
Synthetic rubber (solids) -----	68.9
Sodium silicate (solids) -----	12.8
Soybean protein -----	1.9
Chromic sulphate (hydrate) -----	6.0
Aluminum sulphate (hydrate) -----	20.5

The foregoing beater slurry dispersion was formed into papers of various ream weights using a regular "cylinder machine" type of paper machine. The slurry was pumped from the beater to a beater chest, with addition of water in the usual way to reduce the consistency and aid in the transfer, which raised the pH value; and was then transferred to a machine chest. Just prior to reaching the paper machine, the slurry was mixed with a large amount of water in a mixing box so that the slurry arriving in the cylinder vats (at the wet end of the machine where the pulp is dewatered and formed into sheets) was reduced to a paper-making consist-

ency of 0.5% (percentage by weight of the coated fibers). At this point the pH value was 6.8 (the added water raising the value about that which existed at the end of the beater treatment). A lower value would be desirable and can be obtained by adding acid or a concentrated solution of aluminum sulphate to the slurry at the mixing box, or by operating a closed system in which the white water is recycled for diluting the beater slurry; and this would also permit employment of a higher pH value in the last stage of the beater treatment. Such procedures enable the attaining of a pH value of approximately 4.8 to 5.2 both in the beater and in the cylinder vats, producing a still better deposition and bonding on the fibers and less tendency of the adsorbed latex particles to sluff off into the white water. The cylinder molds were of 60 mesh (but in subsequent work it was found that the 80 mesh size worked better in minimizing loss of material into the white water). The paper was produced at the rate of 70 ft. per minute. It contacted the dryer cylinders for about 5 minutes and was subjected to a temperature of about 220° F., thus causing vulcanization of the rubber phase (which probably was completed thereafter at room temperature). The dried paper was subjected to cold calendaring.

Example 2

This example illustrates a procedure similar to that of the preceding example, chiefly differing in the use of a latex of an acrylate polymer. Hence the description will be given more briefly.

(1) and (2) These steps were the same as in Example 1. The resultant pH value was 4.30 in this case.

(3) 355 pounds of sodium silicate (38% solution) was added (135 lbs. of sodium silicate solids). The resultant pH value was 10.40.

(4) The acrylate polymer latex dispersion consisted of a mixture of two kinds, namely, polyisobutyl acrylate latex (28% solids), and polymethyl-isobutyl acrylate latex (30% solids). 765 lbs. of the former and 1,420 lbs. of the latter were used, providing a total of 640 lbs. of acrylate polymer solids (amounting to 80% of the cellulose paper stock). In this case the protein protective colloid was not added at this point, but subsequently as hereafter described. The resultant pH value was 10.40.

(5) 40 lbs. of chromic sulphate was added, followed by 48 lbs. of gamma soybean protein dispersed in alkaline solution (as described in Example 1), and then 16 lbs. of additional chromic sulphate. After thorough mixing, the resultant pH value was 9.70.

(6) Aluminum sulphate, predissolved in water, was gradually added, with mixing, in amount sufficient to result in a pH value of 5.0.

Example 3

This example also illustrates a procedure similar to that of Example 1, chiefly differing in the use of a Buna-N type of synthetic rubber.

(1) and (2) These steps were the same as in Example 1. The resultant pH value was 3.95 in this case.

(3) Sodium silicate was added in sufficient amount to produce a pH value of 10.25 (252 lbs. of 38% solution).

(4) There was first added 1,400 lbs. of "Hycar OR-15" latex containing 40% by weight of rubber solids. This is a Buna-N type of synthetic rubber formed of the copolymer of butadiene and

acrylonitrile in the ratio of 60:40, and is sold by the B. F. Goodrich Chemical Company, Cleveland, Ohio. There was next added 15 lbs. of "Prosein," dispersed in alkaline solution as described in Example 1. Following this there was added 23.5 lbs. (solid weight) of the dispersed "G-3" vulcanizer composition described in Example 1. The pH value after each of these additions was 10.23.

(5) 24 lbs. of chromic sulphate was mixed in, resulting in a pH of 9.75.

(6) 150 lbs. of aluminum sulphate was added, producing a pH of approximately 4.0.

Example 4

This example illustrates the preparation of a stock which was formed into innersoling and midsoling (useful in making shoes) on a "wet machine" type of paper machine. The procedure was similar to that for Example 1.

(1) and (2) These steps were the same as in Example 1, except that only 8 lbs. of each of the salts were used. The resultant pH value was 4.62.

(3) 162 lbs. of a 38% sodium silicate solution (61.5 lbs. of solids) was used to produce a pH value of 10.08.

(4) 450 lbs. of "GRS No. 3" synthetic rubber latex (38% solids) was used and 8.5 lbs. (dry weight basis) of the "G-3" vulcanizing composition. There was next mixed in 7.5 lbs. of the "Prosein" protein in dispersed form and 1 lb. of sodium hydroxide, resulting in a pH value of 10.30.

(5) There was next added 10 lbs. of water-soluble dye material adapted to produce a tan color in the final sheeting. 10 lbs. of chromic sulphate was added, resulting in a pH value of 9.98. The dye was set on the paper fibers by the salts, acting as mordants.

(6) 65 lbs. of aluminum sulphate was added and the resultant pH value was 4.28.

The slurry was transferred to the wet machine in the usual way and was sheeted out to form, upon drying and calendering, stiff leather-like sheets useful as innersoling and midsoling of shoes.

Example 5

(1) and (2) The procedure was the same as in Example 1.

(3) 252 lbs. of a 38% sodium silicate solution (96 lbs. of solids) was used and resulted in a pH value of 10.5 in this case.

(4) 1,450 lbs. of "GRS No. 3" synthetic rubber latex (38% solids) and 26.5 lbs. (dry weight basis) of the "G-3" vulcanizing composition were used, followed by the addition of 15 lbs. of "Prosein" protein in dispersed form, resulting in a pH value of 10.53.

(5) 24 lbs. of chromic sulphate was added, resulting in a pH value of 10.04.

(6) 125 lbs. of aluminum sulphate was added, resulting in a pH value of 4.0 in the beater.

In this example the transfer of the stock to the cylinder machine (described in connection with Example 1), involved adding sufficient aluminum sulphate (as a 25% solution) to the stock in the mixing box to bring about a pH value of 4.8 at the vat where the fibers are dewatered. This overcame the tendency of the added water to raise the pH value to an undesirably high value after the slurry leaves the beater. This procedure resulted in the fibro-colloidal dispersion being at the optimum pH value at the time of dewatering to make paper, and thereby insured

the best bonding of the rubber particles upon the cellulose fibers and minimized any tendency of the particles to sluff off into the white water.

Among the papers made from this stock was a creped paper having the following physical properties: a caliper thickness of 6.0 mils (0.0060 inch), a lengthwise tensile strength of 12.1 lbs. for a 1/2 inch width test strip, a crosswise tensile strength of 5.0 lbs. per 1/2 inch width, a lengthwise stretch of 20%, and a crosswise stretch of 29%.

Example 6

In this example the beater procedure was similar to that described in connection with the preceding examples except that the sodium silicate was entirely replaced by sodium hydroxide as the alkalizing agent. This change resulted in a much softer type of paper.

(1) and (2) 700 lbs. (dry weight basis) of the paper-making pulp was used, and 21 lbs. each of chromic and aluminum sulphates, resulting in a pH value of 3.70.

(3) 18 lbs. of sodium hydroxide was used to raise the pH value to somewhat over 11.00.

(4) 1,350 lbs. of "GRS No. 3" synthetic rubber latex (38% solids) and 23 lbs. (dry weight basis) of the "G-3" vulcanizing composition were used, followed by the addition of 13 lbs. of "Prosein" protein in dispersed form. The pH value was still somewhat over 11.00.

(5) 21 lbs. of chromic sulphate was added.

(6) A total of 55 lbs. of aluminum sulphate was added, resulting in a pH value of 4.4 in the beater.

As explained in connection with Example 5, additional aluminum sulphate was added in the mixing box to attain a pH value of 4.8 in the stock at the paper-making stage.

Among the papers made from this stock was a creped paper having a caliper thickness of 5.3 mils., lengthwise and crosswise tensile strengths of 4.2 and 3.9 lbs., respectively (for 1/2 inch width test strips), and lengthwise and crosswise stretch values of 20%. A flat uncreped paper was also made which had a caliper of 3.9 mils., lengthwise and crosswise tensile strengths of 10.0 and 4.0 lbs., respectively, and lengthwise and crosswise stretch values of 4% and 12%, respectively.

Example 7

This example illustrates the use of an exceptionally high proportion of synthetic polymer solids, and the use of beaten glassine paper scrap as the fiber stock. The protein protective colloid was omitted. Sodium hydroxide was used as the alkalizing agent. There was obtained a smooth-surfaced, rubbery, translucent sheeting impermeable to oils, water and moisture-vapor.

(1) 700 lbs. of white glassine paper scrap was charged into the beater. Glassine paper is transparent and the fibers are extremely short due to the degrading effect of the treatment employed in making the paper stock. The scrap was given eight hours of hard beating which further reduced the fibers.

(2) 21 lbs. each of chromic and aluminum sulphates were added, resulting in a pH value of 3.8.

(3) 21 lbs. of sodium hydroxide was added, resulting in a pH value of 10.9.

(4) The synthetic latex introduced consisted of 2,545 lbs. of "Geon Plastic Latex" (55% solids), which supplied 1,400 lbs. of solids (200% by

weight of the paper fibers). This material is an aqueous dispersion of a copolymer of vinyl chloride and a minor proportion of vinylidene chloride, which is plasticized with dioctyl phthalate in the proportion by weight of 2 parts polymer and 1 part plasticizer. Each particle contains its own content of polymer and plasticizer. This "Geon" synthetic latex is sold by the B. F. Goodrich Chemical Co., Cleveland, Ohio.

(5) 21 lbs. of chromic sulphate was added.

(6) 80 lbs. of aluminum sulphate was added, resulting in a pH value of 4.0. In order to increase the pH value to more nearly the optimum, there was added 14 lbs. of sodium silicate, resulting in a pH value of 4.4.

As explained in connection with Example 5, additional aluminum sulphate was added in the mixing box to attain a pH value of 4.8 at the paper-making stage. The stock was processed on a cylinder machine and resulted in rubbery, pliable, smooth-surfaced, translucent sheeting. The transparency and smoothness is increased by hard calendering using hot rolls. Maximum transparency can be obtained by using a latex polymer phase which has an index of refraction substantially identical to that of the cellulose fibers.

Example 8

This example illustrates the use of a mixed dispersion of synthetic rubber latex and a rubber-tackifying resin having a strong adhesion to cellulose fibers, which results in depositing upon the fibers a mixture of rubber particles and compatible resin particles capable of blending together to form a rubber-resin flux.

(1) and (2) 700 lbs. of kraft paper-making pulp was used and was given a hard beating for 8 hours; followed by the addition of 21 lbs. each of the chromic and aluminum sulphates.

(3) 223 lbs. of a 38% sodium silicate solution (85 lbs. of solids) was used and resulted in a pH value of 11.1.

(4) 1000 lbs. of "GRS No. 3" synthetic rubber latex (380 lbs. rubber solids), followed by 18.6 lbs. (dry weight basis) of the "G-3" vulcanizing composition, were added. There was also added 245 lbs. of an aqueous dispersion of pentaerythritol ester of rosin (98 lbs. solids), obtained from Hercules Powder Co., followed by the addition of 7 lbs. of "Prosein" protein in dispersed form.

(5) and (6) 21 lbs. of chromic sulphate was added, followed by the addition of 120 lbs. of aluminum sulphate, resulting in a pH value of 4.3 in the beater.

As explained in connection with Example 5, additional aluminum sulphate was added in the mixing box to attain a pH value of 4.8 in the stock at the paper-making stage. The stock ran excellently on the cylinder machine and the paper, while still moist, was creped. The resulting unified creped paper was used in making pressure-sensitive masking tape.

As a variation of the foregoing procedure, in another experiment use was made of a dispersed plasticizer, namely, 123 lbs. of an aqueous dispersion of hydrogenated methyl ester of rosin (49 lbs. solids), obtained from Hercules Powder Co. The proportion of the aqueous dispersion of pentaerythritol ester of rosin was reduced to 123 lbs. (49 lbs. solids). The procedure was otherwise the same and resulted in a stock which ran excellently on the machine.

This example illustrates the preparation of a stock for making a tough wrapping and packaging paper containing both synthetic rubber and asphalt.

(1) and (2) Kraft paper cuttings in the amount of 700 lbs. were given a hard beating for 3 hours; followed by the addition of 10.5 lbs. each of the chromic and aluminum sulphates.

(3) 111 lbs. of a 38% sodium silicate solution (42 lbs. of solids) was added and resulted in a pH value of 10.0. Then 3 lbs. of sodium hydroxide was added to raise the pH value to 10.7.

(4) 140 lbs. of an aqueous dispersion of a soft asphalt (84 lbs. solids) was incorporated, followed by 445 lbs. of "GRS—No. 3" synthetic rubber latex (167 lbs. rubber solids), and 7.3 lbs. (dry weight basis) of the "G-3" vulcanizing composition. There was also added 7 lbs. of "Prosein" protein in dispersed form.

(5) and (6) 21 lbs. of chromic sulphate was added, followed by the addition of 125 lbs. of aluminum sulphate, resulting in a pH value of 3.9.

Additional aluminum sulphate was added to attain a pH value of 4.8 in the stock at the paper-making stage. This stock handled excellently on the cylinder machine.

Having described various embodiments of our invention for purposes of illustration, rather than limitation, what we claim is as follows:

1. A method of preparing an aqueous fibro-colloidal slurry adapted for use in making unified sheet material on a paper-making machine, comprising the steps of: (1) dispersing cellulose paper-making fibers in water to form a fibrous slurry, (2) conditioning the fibers by introducing small proportions of chromic sulphate and aluminum sulphate, (3) alkalizing the slurry to a pH value in the range of 10.0 to about 11.0, (4) admixing a colloidal binder polymer latex, (5) introducing a small additional proportion of chromic sulphate, the amounts of salts thus far introduced being insufficient to deposit the latex particles upon the fibers, (6) introducing aluminum sulphate in sufficient amount to deposit the latex particles upon the fibers and adjusting the pH value to approximately 4.8–5.2.

2. A method of making unified paper having a high rubber content, adapted for use in commercial paper mills, comprising the steps of: (1) beating cellulose fibers in water to form a paper-making beater slurry, (2) conditioning the fibers by introducing small proportions of chromic sulphate and aluminum sulphate, (3) alkalizing the slurry to a pH value in the range of 10.0 to about 11.0, (4) admixing a rubber latex having a solids weight of at least 30% of the dry weight of the fibers, (5) introducing a small additional proportion of chromic sulphate, the amount of salts thus far introduced being insufficient to deposit the latex particles upon the fibers but sufficient to cause a controlled deposition without coagulation in the next step, (6) introducing aluminum sulphate in sufficient amount to deposit the latex particles upon the fibers and adjusting the pH value to 4.0–6.0, and allowing deposition to be completed so that the white water is cleared, (7) diluting the resulting fibro-colloidal slurry with water to paper-making consistency and acidifying to secure a pH value of approximately 4.8–5.2 at the paper-making stage, (8) dewatering the slurry and forming paper on a paper-making machine, the

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white water being clear and substantially free from latex.

3. A method according to claim 2 wherein an alkali-metal silicate is employed for alkalizing in step (3), in sufficient amount to provide at least 5% by weight of SiO_2 relative to the cellulose fibers.

4. A method according to claim 2 wherein a dispersion of a protein protective colloid is incorporated after the introduction of the latex and prior to the final introduction of the aluminum sulphate.

RAYMOND C. McQUISTON;
FRANK E. DAVENPORT.

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