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2,694,633

AFFIXING ORGANIC AND INORGANIC ADDITAMENTS TO CELLULOSIC MATERIALS

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The present invention relates to the affixing of organic and inorganic additaments to fibrous organic and inorganic materials, such as individual fibers, filaments and aggregations of such filaments as felts and woven fabrics, both nitrogenous and non-nitrogenous, such as wool, hair, leather, cellulose and cellulose derivatives, etc.

The art of affixing additaments to fibrous materials is well established, being exemplified by the dyeing of cellulosic filaments and fibers, textiles and the like; by the sizing of paper, both while the fibers constituting the paper are in liquid suspension or by the impregnation of webs of paper; and by the deposition of various materials either upon suspended cellulosic fibers, upon filaments made thereof, or upon the webs and fabrics made therefrom.

A quite common form of affixing additaments to such fibers is by conjoint deposition from suspensions in a liquid, or by impregnation of webs and fabrics by solutions or suspensions of the added substances. However, when such substances are merely in the form of dispersions or solutions it has been the practice to soak or saturate webs of the materials with such solutions, which invariably required the elimination of the solvent employed, or involved the employment of molten materials.

In the art of sizing suspended paper fibers, such as is practiced in the making of paper and molded pulp articles, various substances have been added in the hope that they would attach themselves to the suspended fibers in adequate quantities; but in most cases the amount that could thus be added was quite small. Many attempts to effect the addition of larger amounts, say up to or exceeding 100% by weight on the basis of the cellulose or other fibrous material, have been made, but have been unsuccessful.

It is therefore one of the primary objects of the present invention to provide methods for the affixing of additaments to fibrous materials under conditions such that extremely large amounts of the added substances can become firmly and substantially irremovably attached and secured to the fibrous material.

A further object of the present invention is to condition fibrous material so that they will very strongly attract to themselves additaments comprising an extremely varied group of materials, which includes both organic as well as inorganic substances, such as sizing materials, waterproofing materials, fireproofing materials, coloring matter, dyes, pigments and fillers, plasticizers, toxics, and substances which are capable of altering the properties of the material to which they have become affixed.

Still a further object of the present invention is to condition the additaments so that they will form cationically active emulsions or suspensions of a nature enabling the water-insoluble material contained in the emulsions or suspensions to attach itself to fibrous materials with great tenacity.

Another object is to treat the material with cationically active surface-active, water-insoluble but water-dispersible substances having at least one hydrophobic group so that when subsequently a cationically active emulsion or dispersion of the additament is allowed to act upon the so treated material, the additament is firmly and substantially irremovably affixed thereto.

The term additament will be used in the present specification and claims as the broad and proper generic term for any substance that may, by the processes of the present invention, become affixed to the treated fibrous

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material, and the term includes such diverse materials as inorganic pigments, fillers and weighting materials, as well as organic resins, elastomers, polymers, plastics, etc. Among the materials which can be affixed to the fibrous material by the processes and means of the present invention are the following:

(1) Loading and filling materials, e. g. clays, diatomaceous earths, pigments, etc.;

(2) Coloring materials, e. g. pigment-colors and dye-stuffs;

(3) Sizing materials, e. g. glues, resins, gums, starches, casein and other proteinaceous substances;

(4) Plasticizing materials, e. g. oils, waxes, plasticizers, etc.;

(5) Varnish materials, such as phenolic resin varnishes, alkyd resins, polyvinyl ester polymerization products, a great diversity of synthetic resins, elastomers such as natural or synthetic rubbers, and similar substances; cellulose esters and ethers, etc.;

(6) Unusual materials of high technical utility, e. g. chlorinated paraffins; chlorinated elastomers; anti-toxic, anti-fungus materials, preservatives, toxic substances and the like, even including subdivided metals.

It will be understood from a study of the more detailed description to follow, that there is substantially no limitation to the type of substances which may be combined with treated materials, provided that such substances be water-insoluble and capable of being formulated into a cationically reactive dispersion or emulsion, the particles whereof carry a high cationic i. e. an electro-positive charge. The amount of such addition is governed by the characteristics of the material and by the degree of the cationic reactivity of the dispersion or emulsion, and the addition is substantially quantitative, there almost always being no uncombined or unretained material, provided the process is carried out within the teachings of the present invention.

By reason of the importance of the present contribution, particularly to the cellulosic material-fabricating arts, it will necessarily have to be exemplified by a large number of diverse examples, so that the true generic nature of the invention will be properly evaluated, and the generic claims hereunto appended be supported by sufficient data to warrant them.

Although the present process was initially developed for use in the paper and paperboard industry, where the cellulosic fibers are carried in aqueous dispersions until the paper or paperboard is formed into a web on the conventional equipment used for such production, extended studies have established the fact that the present process is likewise equally adaptable to pulp-molding processes and to the treatment of textile threads, yarns, and felted or woven fabrics, treatment of inorganic fibers, leather materials, woolen threads, yarns, and fabrics, etc.

While most of the examples hereinafter to be recited deal with the art of papermaking or the production of paperboard, insulation board, etc., it must be understood at the very outset that the invention is not to be limited thereby.

The present invention therefore primarily relates to the making of webs or forms of cellulosic fibers, notably paper, paperboard, and similar paper products by the usual paper-making procedures, as typified by the conventional single and multi-vat cylinder machines, Yankee, Harper, Fourdrinier, and wet machines; and fiber-molded forms as made in conventional pulp or fiber-molding devices.

One of the most useful applications of the present invention is to combine quantitatively with cellulosic fibers in aqueous suspension, and prior to their formation into cellulosic webs or forms, any type of water-insoluble material that is adaptable to formulation into a cationically reactive dispersion or emulsion, the water-insoluble particles of which are electro-positively reactive.

The fundamental basis of the present invention involves the pre-treatment or conditioning of the fibrous material with a water-insoluble but water-dispersible, highly polar, cationically active surface-active agent containing at least one hydrophobic group. This is carried out by means of either aqueous dispersions of such

materials, or by the treatment of the fibrous material while in aqueous suspension with a dispersion or solution of the conditioning agent (as it will hereinafter be termed for sake of conciseness of expression), such solution or dispersion preferably being in an organic solvent that may or may not be miscible with water. It appears that, by reason of the polar nature of these conditioning materials, a sufficient amount of the conditioning material, even when contained in the dissolved state in an organic non-water-miscible solvent, will pass into the aqueous phase so as to enable it to act upon or to react with the fibrous materials, so as to place them into the proper condition for the subsequent treatment by means of which the desired additament is affixed thereto.

The affixation of the additament is brought about by mixing an aqueous suspension of, for example, a cellulosic material with an emulsion or suspension of the additament, which latter is contained as the disperse phase in a dispersion of a long-chain amide-amine salt, such as will hereinafter be more specifically enumerated. When suspended in a dispersion of such a salt, which itself is insoluble in water, the particles of the dispersion, irrespective of the nature of the dispersed material, will have a positive electrical charge, which ordinarily is expressed herein by stating that the emulsion or dispersion is "cationically active" or "cationically reactive."

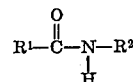
Broadly speaking, the determination of the amounts of the conditioning material required, and of the amounts of the additaments which may be affixed to the fibrous material, may be readily ascertained by analytical methods involving electrometric titrations of, first, the suspended fibrous material with the conditioning agent, and then the electrometric titration of a fixed amount of a suspension of the conditioned material with an emulsion or suspension of the additament of known concentration. The amount of reagents then used in the practical application of the present invention may then readily be calculated.

Thus, for example, a given weight of cellulosic material, the exact bone-dry weight of which is known, may be suspended in a known amount of water, whereafter the suspension thus obtained is titrated with a volumetric suspension of the conditioning agent, that is to say, with a solution or suspension of the conditioning agent having a definitely known concentration. The changes in the hydrogen-ion concentration of the suspension is monitored by means of the usual glass electrode of a sensitive potentiometer assembly, so that the optimum amounts of addition of the conditioning agent may be ascertained. In the same way, the thus treated suspension is then further titrated with the suspension or emulsion of the additament.

The conditioning materials or agents can be rather broadly designated as being water-insoluble cationically active surface-active substances, which contain at least one hydrophobic group but which have some degree of dispersibility in water. They must, moreover, also be polar to a considerable degree, and generally speaking, the greater the polarity, the better is the conditioning effect. Conditioning agents which contain a heterocyclic group containing nitrogen, which group is directly connected with a hydrophobic group, have been found to be particularly effective. Another group of effective conditioning agents includes substances in which the hydrophobic group is joined to the cationic group through an intermediate linkage, e. g. an amide linkage, an ester linkage, an ether or related linkage, a sulfide or sulfone linkage, or an imino linkage. Surface-active phosphorus compounds have also been found to be highly useful. Another group contains basic nitrogen joined directly to the hydrophobic group, i. e. amines which are dispersible in, but not really soluble in water. Nitriles, dinitriles, dialkylcyanamides may also be used as conditioning agents. Examples of each of these generic groups will be given.

One example of a highly operable cationically reactive surface-active agent employed in the first or conditioning step of the present process, comprises a cationically reactive material resulting from the reaction products formed by the addition of water-soluble amines or readily water-dispersible amines, preferably lower aliphatic amines, to the oxidation products formed by the liquid phase oxidation of normally liquid fractions of petroleum, e. g., 36-40° Baumé fuel oils, or 45° distillate, or steam distillates of these oxidation products, said oxidation

products or steam distillates therefrom being rich in aliphatic carboxylic acids containing from 10 to 16 carbon atoms (the average being 12 carbon atoms) per aliphatic chain. U. S. Patents Nos. 2,330,524 and 2,330,525 are illustrative of operable methods of producing such amine-acid reaction products. These compounds may be considered as being substituted amides having the general formula



in which R¹ is an aliphatic group having from about 8 to about 20 carbon atoms, and R² is an alkyl group having from about 4 to 10 carbon atoms. The products are substantially insoluble, non-ionizable, and non-dissociable in water but may be used in the form of dispersions.

Such materials of which there are presently five types available, are known commercially as "Alox L-1205-X," "Alox 1561," "Alox 1560," "Alox 1650," and "Alox 1651."

The electrometric titration of cellulosic fibers in aqueous suspension with the cationically reactive surface-active agents, gives typical titration curves, as will be further explained. A change in hydrogen-ion concentration is characteristic, and succeeding added increments of such materials will lead to a condition until a point is reached at which no further reaction is apparently effected.

A typical electrometric titration data table is shown below. The electrometric titration data is one of the criteria of the operability of the cationically reactive surface-active agent selected for use.

The cellulose fiber used in this particular evaluation was a fully bleached kraft pulp, the pulp freeness factor thereof being about 600 Canadian standard. The particular cationically reactive surface-active agent used, on an "as is" basis was "Alox L-1205-X" (a product of the reaction of an amine with a monobasic acid as hereinbefore stated). The fiber suspension was an exact 1% on the bone-dry basis, the suspension weight being an exact 1,000 grams.

TABLE I

Cc. "as is" basis cationically reactive surface-active agent added (Alox L-1205-X)	pH value of cellulose suspension after addition	Visual condition of liquid phase of cellulose suspension
0	7.30	clear.
0.20	7.20	Do.
0.40	6.60	Do.
0.60	6.50	Do.
0.80	6.40	Do.
1.00	6.30	Do.
1.20	6.20	Do.
1.40	6.15	Do.
1.60	6.05	Do.
1.80	6.00	Do.
2.00	5.90	olly rings form.
2.20	5.90	olly rings.
2.40	5.90	Do.
2.60	5.90	olly surface.
2.80	5.90	black oolly surface.
3.00	5.90	Do.
3.20	5.90	Do.
3.40	5.90	Do.
3.60	5.90	Do.
3.80	5.90	Do.
4.00	5.90	Do.
4.20	5.90	Do.
4.40	5.90	Do.
4.60	5.90	Do.
4.80	5.90	Do.
5.00	5.90	Do.

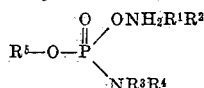
The end point of reactivity was sharp (at about pH 6.0), not only as indicated by the pH value, but by visual observation of the liquid phase condition as well. It thus appears that a definite amount of the conditioning agent is fixed or adsorbed by the cellulosic fibers in this particular case.

Another example of an operable cationally reactive surface-active agent which may be employed in the first or conditioning step of the process is an alkyl amine salt of an alkyl amide of an alkyl phosphoric acid, having the structural formula as shown below. This material likewise has a long aliphatic chain.

This material is of a type fully described in United

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States Patent No. 2,406,423 as a surface-active composition consisting essentially of the formula



in which R^1 , R^2 and R^4 represent a radical of the class consisting of hydrogen and an alkyl group. R^3 represents an alkyl group of at least 8 carbon atom chain length, and R^5 represents an alkyl group of 1 to 4 carbon atoms chain length. These substances are long chain aliphatic amine salts of a long chain aliphatic amide of a short chain alkyl ester of orthophosphoric acid obtained by reacting one mol proportion of a neutral alkyl ester of metaphosphoric acid in which the alkyl group contains from 1 to 4 carbon atoms with one mol proportion of each of two aliphatic amines in which at least one of the amines has an aliphatic radical containing a straight chain of at least 8 carbon atoms. Thus the amine may be a lauryl amine or a stearyl amine.

The R^1 and R^2 may be ethyl groups. A particularly useful compound, and the one used in many of the subjoined examples, is the monolauryl amine salt of the monolauryl amide of ethyl phosphoric acid. It is commercially known as "Victamine C."

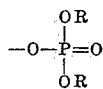
This material is but very slightly soluble in water, the water-solubilizing group being the alkyl group. It does not have, when in water dispersion, the surface-active properties of the "Alox" materials, but nevertheless is most efficient in the combination of relatively large amounts of water-insoluble materials with cellulosic fibers treated with it in aqueous suspension.

This material is soluble in methanol, toluene, ether, kerosene, and similar hydrocarbons, and toluene solutions of it exhibit very appreciably increased reactivity with cellulosic fibers in aqueous suspension. Toluene itself has a surface-active action, and the composite of the water-insoluble cationically reactive lauryl amine salt of the lauryl amide of ethyl phosphoric acid with toluene makes for a most effective cationically reactive surface-active agent, as is evidenced by the pair of electrometric titration data tables relative to this material, the pulp that was electrometrically titrated being from the same beater of fully bleached kraft pulp as was used in the evaluation of the already mentioned "Alox" material.

In this instance a polybasic acid is the starting point of the amine reaction, and there is a polyvalent cation with a high degree of electropositivity, and a 12 carbon atom chain in the alkyl group. As distinguished from the "Alox" type of materials, this cationically reactive material is practically odorless and light tan in color, as contrasted to the deep black of the "Alox" materials, and not as oily in appearance.

The composite reagent, made by dissolving the cationically reactive material in a non-ionic organic type of surface-active agent, such as toluene, produces a most effective operable conditioning material for the first step in the operation of the present invention. The evaluation data of this type of reagent is detailed subsequently.

While a toluene solution of the "Victamine C" is highly suitable, there is another way of using this substance, and that is in conjunction with a non-ionic liquid wetting agent, such, for example, one known as "Victawet 12," which has the general formula of medium chain alkyl group



R being a hydrophilic group, and which is furnished in the form of a liquid having a specific gravity of 1.121 at 28°C ., and which is soluble in alcohols, acetone, toluene, etc., but merely forms a milky suspension in water. The liquid "Victawet 12" is a solvent or diluent for the "Victamine C." Thus the "Victamine C" may be dissolved in "Victawet," and the resulting solution incorporated with an aqueous suspension of cellulosic fibers, as in a beater or similar instrumentality, and the process then being continued as outlined.

In carrying out the processes of the present invention, cellulosic fibers that have been treated with an amount of a cationically active surface-active agent of the desired type, as indicated by a preliminary electrometric

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titration as above mentioned, are subjected while in aqueous suspension, as in a beater, to the action of an emulsion or dispersion of the additament, which latter emulsion or dispersion has also been rendered cationically reactive by the addition, for example, of a salt of a long chain fatty acid amine, preferably one having a 16 to 20 carbon atom chain. Substantially immediately after the addition of such an emulsion, the previously suspended material of the emulsion will attach itself to the cellulosic fibers with a degree of tenacity that is truly remarkable. The liquid in which the materials are suspended will become quite clear, and the adsorption or affixation of the suspended material upon the treated cellulosic fibers is substantially quantitative, and may equal, or even exceed, 100 per cent by weight of the bone-dry weight of the cellulosic fibers.

For a better understanding of the present invention, the following examples are given. The earlier examples will be given in greater detail, and the other examples then sketched in, with the understanding that similar manipulative details are employed. The later examples are therefore more in the nature of stated results, using different materials and proportions; but generally speaking, procedurally they are equivalent to the earlier examples. While only about eighty or so actual examples are given to demonstrate the truly generic nature of the present invention, it can be stated that well over 350 examples have been carried out successfully, not only on a laboratory basis but on a Fourdrinier machine.

EXAMPLE 1

360 grams of bone-dry fully bleached southern kraft pulp were furnished to a laboratory beater, and the stock well brushed out, after which 25.20 grams of "Alox L-1205-X" were added to the beater furnish, and the beating continued for one and one-half hours to a finished beater freeness of 680 (Canadian standard). The finished beater consistency was 1.50% (bone-dry basis) and the pH value of the beater stock was 8.40.

662 grams of beater stock as above prepared were weighed out and 338 grams of water added to give an exact 1% bone-dry suspension of "Alox"-treated cellulosic fibers. This suspension of treated cellulosic fibers was electrometrically titrated with a 20% non-volatile-solids emulsion of polymerized rosin, the emulsion being cationically reactive. The rosin used has the trade name designation of "polypale rosin." The electrometric titration data is tabulated below.

cc. 20% N. V. Solids Cationically Reactive Polymerized Rosin Emulsion Added	pH Value after Emulsion Addition	Visual Appearance of Liquid Phase of Suspension
0.....	8.40	clear liquid.
10.....	8.40	Do.
20.....	8.40	Do.
30.....	8.25	Do.
40.....	8.20	Do.
50.....	8.15	Do.

The rosin solids added to the treated cellulosic fibers equalled 10.00 grams. At the end of the titration cycle a hand sheet was made, which gave no evidence of sticking on the forming wire, press felts, or dryer surfaces, and no foam was in evidence. The white-water from the forming wire was crystal clear and completely free from fiber or rosin particles. The hand sheet was dried to a constant weight at 215°F ., and the weight recorded.

A second sample of exactly 662 grams of beater stock was weighed out, and 338 grams of water added thereto, and a hand sheet made of this fiber suspension. The sheet was dried to a constant weight at 215°F . and the weight recorded. The results were as follows:

Bone-dry weight of cellulose-rosin hand sheet=20.15 grams

Bone-dry weight of blank cellulose sheet=10.10 grams

Bone-dry weight of rosin solids added=10.00 grams

Bone-dry weight of rosin solids plus bone-dry blank=20.10 grams

Percentage rosin solids added=100% on the cellulose weight

Percentage rosin solids combined with cellulose=100%

Example 2

360 grams, bone-dry basis, of unbleached southern kraft pulp were furnished to the laboratory beater, and the stock well brushed for one-half hour, whereafter 28.80 grams of "Alox L-1205-X" were added and the beating continued for one hour to complete the beating cycle. The finished beater freeness was 580; the bone-dry beater consistency was 1.55%. Thereafter a series of standard 10.00 gram (bone-dry basis) fiber suspensions were made up at exactly 1% treated fiber consistency, and various of the prepared samples were treated with different types of cationically reactive emulsions of water-insoluble materials, the said emulsions being used at a 2% solids concentration. A series of blank hand sheets were made from this treated beater stock, to use in the evaluation of the quantitative factors of combination of treated cellulosic fibers and cationically reactive emulsions or dispersions of the water-insoluble additament. The average bone-dry weight of the blank hand sheets of this treated stock was 10.50 grams, which figure is used in the series of evaluation studies made of this beater furnish.

To one of the standard 1% treated fiber suspensions containing 10.00 grams of treated cellulosic fiber was added 250 cc. of a 2% non-volatile solids emulsion of "G. R. I.-70" rubber, which is an isoprene-isobutylene type of synthetic rubber, the rubber emulsion being cationically reactive. A complete and instantaneous combination of the added rubber and the treated cellulosic fibers took place, the liquid phase of the suspension of the mixture clearing instantly after the addition of the cationically reactive emulsion. A hand sheet was made of the reacted mixture. No sticking tendencies were observed on the forming wire, press felts, or dryer faces, and the white-water from the forming wire was crystal clear and completely free from fibrous or rubber particles. The hand sheet was dried to a constant weight at 215° F. and the weight recorded. The results were as follows:

Bone-dry weight cellulose "G. R. I.-70" rubber sheet	grams	15.40
Bone-dry weight blank sheet	do	10.50
Bone-dry weight "G. R. I.-70" rubber added	grams	5.00
Percentage of "G. R. I.-70" rubber added	per cent	50
Percentage "G. R. I.-70" rubber combined with treated cellulose	per cent	98

EXAMPLE 3

To one of the standard 1% treated fiber suspensions of the above beater furnish containing 10.00 grams (bone dry) of treated cellulosic fibers, exactly 500 cc. of a 2% non-volatile solids emulsion of "Piccoumaron-S-115" (coumarone-indene) resin was added, the resin emulsion being cationically reactive. An instantaneous combination of the cationically reactive coumarone-indene resin emulsion and the treated cellulosic fibers took place, the liquid phase of the reacted mixture becoming crystal clear immediately after the addition of the cationically reactive coumarone-indene resin emulsion. A hand sheet was made of the reacted mixture. No sticking tendency was observed on either the forming wire, press felts, or dryer faces, and the white-water draining from the sheet forming wire was crystal clear and free from either fibrous or resinous matter. The hand sheet was dried to constant weight at 215° F. The results were as follows:

Bone-dry weight resin solids added	grams	10.00
Bone-dry weight blank hand sheet	do	10.50
Bone-dry weight processed sheet	do	21.50
Percentage coumarone-indene resin solids added	per cent	100
Percentage coumarone-indene resin solids combined with the fiber	per cent	100

EXAMPLE 4

To one of the standard 1% treated fiber suspensions of the above beater furnish containing 10.00 grams of bone-dry treated fiber, 500 cc. of a 2% non-volatile solids, cationically reactive emulsion of chlorinated paraffin was added. An instantaneous combination of the cationically reactive emulsion of chlorinated paraffin and the treated cellulosic fibers took place, the liquid phase of the mixture clearing immediately after the addition of the

emulsion. A hand sheet was made of the reacted mixture. There was no evidence of sticking to the forming wire, press felts, or dryer faces, and the sheet was dried to a constant bone-dry weight and the weight recorded. The white-water draining from the forming wire was completely free of fibrous or water-insoluble particles, being crystal clear. The dried sheet was quite flame resistant, as would be expected. The results were as follows:

Bone-dry weight of chlorinated paraffin added	grams	10.00
Bone-dry weight blank hand sheet	do	10.50
Bone-dry weight chlorinated paraffin cellulose sheet	grams	20.70
Percentage chlorinated paraffin solids added	per cent	100
Percentage chlorinated paraffin solids combined with fiber	per cent	100

EXAMPLE 5

To one of the standard 1% treated fiber suspensions of the above beater furnish, 700 cc. of a 2% solids content cationically reactive emulsion of an hydrogenated esterified rosin were added. An instantaneous combination of the cationically reactive emulsion and the treated cellulosic fibers was effected, and directly after the addition of the cationically reactive emulsion, the liquid phase of the reacted mixture became crystal clear. A hand sheet was made of the reacted mixture, and at no point in the processing of the hand sheet did any sticking occur. The white-water from the forming wire was free from fibrous and resinous material and was crystal clear. The hand sheet was dried to a constant bone-dry weight and the weight recorded. The results were as follows:

Bone-dry weight hydrogenated esterified rosin added	grams	14.00
Bone-dry weight blank hand sheet	do	10.50
Bone-dry weight hydrogenated esterified rosin cellulose fiber complex hand sheet	grams	25.00
Percentage hydrogenated esterified rosin added	per cent	140
Percentage combination hydrogenated esterified rosin with fiber	per cent	100

The hand sheet made was placed in a small laminating press to flow the complex of hydrogenated esterified rosin and cellulosic fibers. The temperature of the platens was set at 260° F., the sheet placed between the heated platens, and about 800 p. s. i. pressure applied to the press. Contact time was about 10 seconds. The press was opened while still hot, and the flowed complex sheet removed from the platens. There was no evidence of sticking, no evidence of flash or beading on the sheet edges, and the flowed sheet was completely translucent.

EXAMPLE 6

To one of the standard 1% treated fiber suspensions of the above beater furnish, exactly 500 cc. of a 2% non-volatile solids cationically reactive emulsion of methylmethacrylate resin were added. An instantaneous combination of the cationically reactive resin emulsion and the treated cellulosic fibers was effected, the liquid phase of the reacted mixture clearing immediately after the addition of the emulsion. A hand sheet was made of the reacted mixture. No evidence of sticking was noticed on the sheet forming wire, the press felts, or the dryer faces, and the sheet was dried to constant bone-dry weight and the weight recorded. The white-water draining from the forming wire was crystal clear and completely free from either fibrous or resin particles. The results were as follows:

Bone-dry weight methylmethacrylate resin solids added	grams	10.00
Bone-dry weight blank hand sheet	do	10.50
Bone-dry weight methylmethacrylate cellulose sheet	grams	20.70
Percentage methylmethacrylate resin added	per cent	100
Percentage combination methylmethacrylate resin with fiber	per cent	100

The dried hand sheet was extremely tough and felt like rawhide. The possibility of this specific quantitative combination of treated cellulosic fibers and a poly-methyl-

methacrylate resin in the formulation of artificial leather is of importance, as the finished hand sheet exhibited many of the characteristics of such material.

EXAMPLE 7

This example is one of the most striking ones made of record in connection with the present invention. To one of the standard 1% treated fiber suspensions of the above beater furnish, exactly 500 cc. of a 2% non-volatile solids cationically reactive dispersion of chrome yellow pigment (a commercial pigment product marketed under the trade name of C. P. Chrome Yellow Medium No. 1085, of the lead chromate type) were added. An instantaneous combination with the treated cellulosic fibers was effected, the liquid phase of the reacted mixture becoming crystal clear and completely free from color. There was no settling of chrome pigment at the bottom of the reaction vessel notwithstanding the fact that the specific gravity of the chrome yellow pigment is 5.90. A hand sheet was made of the reacted mixture and dried to bone-dry weight. A new set of blank hand sheets was made and the average weights (bone dry) determined and recorded. There was no evidence of sticking on the forming wire, the press felts, or the dryer surfaces, and the white-water draining from the forming wire was completely colorless and free from any trace of either fiber or pigment. The results were as follows:

Bone-dry weight chrome yellow pigment added	grams--	10.00
Bone-dry weight blank hand sheet.....do.....	11.20	
Bone-dry weight chrome yellow-cellulose fiber complex.....do.....	grams--	21.50
Percentage chrome yellow pigment added	percent--	100
Percentage chrome yellow pigment combined with fibers.....do.....	percent--	100

This is a most striking example of quantitative combination of treated cellulosic fibers with water-insoluble inorganic materials by the methods of the present invention.

EXAMPLE 8

500 grams of bone-dry, full bleached, southern kraft pulp were furnished to the laboratory beater, and after the stock had been well brushed out, 90 cc. of "Alox L-1205-X" were added to the beater furnish and the reaction continued for a period of five minutes. Thereafter an exact 1% bone-dry treated fiber suspension of the so treated beater stock was made up, and 1000 grams of such suspension, corresponding to exactly 10.00 grams of bone-dry treated fiber, made up for evaluation. To this fiber suspension of the beater stock 250 cc. of a 2% non-volatile solids content, cationically reactive emulsion of an acrylonitrile-butadiene elastomeric copolymer were added. This material was a product of the B. F. Goodrich Chemical Company and is identified in the trade as "HyCar-OR-25-1502-X362." The reaction time for combination with the treated cellulosic fibers was of a much slower order than had been the case with other types of cationically reactive dispersions or emulsions, but in a matter of from one to two minutes the liquid phase of the reacted mixture completely cleared, and a hand sheet was made. The elastomeric complex of cellulose and acrylonitrile-butadiene was extremely free on the wire, gave no evidence of sticking on the forming wire, the press felts, or the dryer surface, and the white-water draining from the forming wire was crystal clear and completely free from fibrous or resin particles. The hand sheet was dried to constant bone-dry weight and the weight recorded. The dried sheet was extremely tough and rubberlike and had great tearing resistance. It readily lends itself to the machine production of rubberized material for the manufacture of bags and wrappings. The results were as follows:

Bone-dry weight acrylonitrile-butadiene added	grams--	5.00
Bone-dry weight blank hand sheet.....do.....	10.00	
Bone-dry weight acrylonitrile-butadiene fiber complex.....do.....	grams--	15.00
Percentage acrylonitrile-butadiene added.....do.....	percent--	50
Percentage acrylonitrile-butadiene combined with fiber.....do.....	percent--	100

EXAMPLE 9

500 grams, bone-dry basis, of full bleached southern kraft pulp were furnished to the laboratory beater, and

after the stock had been well brushed for one half hour, exactly 15.00 grams of "Victamine C" (solids basis), in the form of a 5% aqueous dispersion, and being a cationically reactive surface-active agent as already explained, were added to the beater and the beating continued for an added one and one-half hours to an approximate finished beater freeness of 600, Canadian standard. Thereafter the bone-dry beater consistency was determined and a series of standard 1% bone-dry treated fiber suspensions made up for evaluation work, each such suspension totalling 1000 grams in weight and containing 10.00 grams of treated bone-dry fiber.

To one of these standard 1% Victamine treated cellulosic fiber suspensions exactly 250 cc. of a 2% non-volatile solids content cationically reactive emulsion of acrylonitrile-butadiene elastomeric polymer were added, and an instantaneous combination with the treated cellulosic fibers was effected, far more rapid in reaction than was the case in Example 8. The liquid phase of the treated cellulosic suspension became clear immediately after the addition of the cationically reactive emulsion of the elastomeric copolymeric product. A hand sheet was made and there was no evidence of sticking at any point in processing. The treated cellulosic fibers were very free on the forming wire and dried readily. The sheet was tough and rubberlike when cured at 310° F. and exhibited great tearing resistance. The combination of acrylonitrile-butadiene elastomer with the treated cellulosic fibers was completely quantitative. The white-water from the wire was crystal clear and completely free from fibrous and rubber particles. The retention, when tested in the manner hereinabove frequently explained, was substantially 100 per cent.

EXAMPLE 10

To one of the standard 1% treated fiber suspensions of the above Victamine C treated beater furnish exactly 500 cc. of a 2% non-volatile solids content cationically reactive mixed emulsion were added, being made up of 75% of hydrogenated ester gum solids and 25% of acrylonitrile-butadiene solids. An instantaneous combination was effected between the emulsion and the treated cellulosic fibers, the liquid phase of the reacted mixture clearing immediately upon the addition of the emulsions. A hand sheet was made of the reacted mixture. No evidence of sticking was observed at any point in the manufacture of the hand sheet; the white-water draining from the forming wire was crystal clear and completely free from fibrous or resin particles. The combination of the combined cationically reactive emulsions and the treated cellulosic fibers was completely quantitative.

The finished hand sheet thus made was, after drying, placed in a small laminating press to compress the sheet and apply heat thereto such as would obtain in a die-stamping operation. About 320° F. was maintained in the press, with a platen pressure of about 800 p. s. i. The finished sheet is useful as a base material for the die-stamping of disposable plates. The hand sheet time in the laminating press was in excess of one minute. The cured sheet, as removed from the press, showed no evidence of sticking to the press platens and no evidence of extrusion or beading of resin on the sheet edges. The cured sheet withstood penetration by cottonseed oil for an excess of 30 minutes at 160° F., and thus is shown to be an excellent grease-resistant material.

EXAMPLE 11

500 grams, bone-dry basis, of full bleached southern kraft pulp were furnished to the laboratory beater, and after the stock had been well brushed for one-half hour, 50 grams of "Alox 1561," a cationically reactive surface-active agent, were added and the beating continued for one and one-half hours to give a beater freeness of about 600, Canadian standard. Thereafter standard 1% treated fiber suspensions of the so-treated material were made up (bone-dry treated fiber basis), each standard fiber suspension equalling 1000 grams or 10.00 grams of bone-dry treated fiber.

One of these standard 1% "Alox 1561" treated fiber suspensions of the beater stock was electrometrically titrated with a 5% "Valspar" (spar) varnish solids in the form of a cationically reactive emulsion, the data of which is tabulated below. A commercial purchase of Valspar varnish was made and the non-volatile solids con-

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tent thereof determined to be approximately 40%. The varnish was cut with acetone, a suitable cationic emulsifier was added, and the solvated varnish and cationic emulsifier added to water by means of a colloid mill to make a 5% varnish solids type of emulsion which was highly cationically reactive. This was used as the titrating medium in the electrometric titration of a standard 1% "Alox 1561" treated (bone dry) cellulosic fiber suspension, containing 10.00 grams of bone-dry cellulosic fiber.

cc. of 5% "Valspar" varnish solids cationically reactive emulsion added	pH value after addition of cationically reactive "Valspar" varnish emulsion	Visual appearance of liquid phase after addition ¹
0.....	7.50	clear.
25.....	7.00	instantaneous combination.
50.....	6.80	Do.
75.....	6.40	Do.
100.....	6.20	Do.
125.....	6.00	Do.
150.....	5.90	Do.
175.....	5.80	Do.
200.....	5.80	Do.

¹ Liquid phase completely clear 2 to 3 seconds after each addition.

A hand sheet was made at the end of the titration cycle. An excellent sheet was formed, there being no indication of sticking to either forming wire, press felts, or dryer surfaces. The hand sheet was dried to bone-dry weight and to a constant weight to eliminate drying oils, the cationically reactive "Valspar" varnish emulsion being based on "Valspar" varnish solids. The white water draining from the forming wire was crystal clear and free from fibrous and solid particles. The sheet was then dried at 310° F. to insure loss of volatiles. A blank hand sheet was made of a duplicate 1% treated cellulosic fiber suspension for comparison. The results were:

Bone-dry weight "Valspar" varnish solids added	grams--	10.00
Bone-dry weight blank hand sheet	do----	10.00
Bone-dry (310° F.) varnish-cellulose complex	grams--	20.30
Percentage "Valspar" varnish solids added	per cent--	100
Percentage varnish combination with cellulose fibers	per cent--	100

The practical application of this procedure is in the machine production of insulating papers, using a phenolic varnish of high dielectric properties, as against present methods of such production by methods of saturation and coating applications. The finished sheet was extremely flexible, quite tough, and highly resistant to penetration by water.

EXAMPLE 12

500 grams of bone-dry, unbleached kraft pulp were furnished to the laboratory beater, and the stock well brushed. Thereafter 25.00 grams ("as is") of "Alox L-1205-X" were added and the beater circulated for an additional one and one-half hours with a hard roll action to effect a hard beating action and to complete the reaction cycle for the "Alox L-1205-X". Thereafter a series of standard 1% bone-dry Alox-treated fiber suspensions were prepared for evaluations, each suspension weighing exactly 1000 grams and containing approximately 10.00 grams of bone-dry treated cellulosic fiber. The finished beater consistency on a bone-dry basis was 1.55% and the freeness factor approximately 500 Canadian standard. The pH value of the finished beater was 6.40. A series of blank hand sheets were made to establish an average bone-dry weight of the fibrous content of the 1% standard cellulosic fiber suspensions. The average weight of the blank hand sheets was 10.60 grams; the variation was not over 0.20 grams in the weight of several blank hand sheets.

To one of these standard 1% treated fiber suspensions (bone-dry basis) were added 500 cc. of a 2% non-volatile solids content cationically reactive emulsion of a paratertiarybutylphenolformaldehyde resin. An instantaneous combination of the added resinous material was effected with the treated cellulosic fibers, the liquid phase

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clearing immediately after the addition of the emulsion. A hand sheet was made of the reaction product. No sticking was evidenced at any point in the processing of the hand sheet, the white water draining from the forming wire being crystal clear and free from fibrous and resinous particles. The sheet was dried to constant weight and the weight recorded, the results being as follows:

10	Bone-dry weight of paratertiarybutylphenolformaldehyde resin	grams--	10.00
	Bone-dry weight blank hand sheet (average)	do----	10.00
	Bone-dry weight paratertiarybutylphenolformaldehyde resin, cellulosic fiber complex	grams--	20.90
15	Percentage of paratertiarybutylphenolformaldehyde resin added	per cent--	100
	Percentage combination of added resinous material with fibers	per cent--	100

EXAMPLE 13

To one of the standard 1% treated fiber suspensions from the treated beater stock of Example 12, 500 cc. of a 2% non-volatile solids cationically reactive emulsion of a high melting point paraffin wax were added. An instantaneous combination of the added wax materials with the treated cellulosic fibers was effected, the liquid phase clearing immediately after the addition of the emulsion. A hand sheet was made of the reaction product. No sticking tendencies were evidenced on either the forming wire, the press felts, or the dryer surfaces, and the white water draining from the forming wire was crystal clear and completely free from fibrous and wax particles. The sheet was dried to constant weight. The hand sheet was extremely soft and flexible, highly resistant to penetration by water, and very translucent and free from tack. The quantitative data are as follows:

	Bone-dry weight of wax added	grams--	10.00
	Bone-dry weight of blank hand sheet (average)	do----	10.60
	Constant weight of cellulose-wax complex	do----	20.75
	Percentage of wax solids added	per cent--	100
45	Percentage of wax solids combination with fibers	do----	100

This sheet offers interesting possibilities in the use of waxes on the paper or molding machine, as contrasted to the impregnation of paper sheets subsequent to manufacture by means of a waxing operation, such as saturation, dipping, or coating methods, and offers also the possibilities of wax-rosin combinations in paper production for the manufacture of highly sized materials that are not possible to produce today by the present conventional methods of coagulation and precipitation.

Further generalizations

Instead of the particular forms of cellulose mentioned in the above fourteen examples, any of the following cellulosic fibers, or mixtures thereof, may be successfully employed: unbleached kraft pulp, semibleached kraft pulp, full bleached kraft pulp, unbleached sulfite pulp, semibleached sulfite pulp, full bleached sulfite pulp, unbleached semichemical pulp, semibleached semichemical pulp, caustic cooked chestnut fiber, unbleached soda pulp, semibleached soda pulp, full bleached soda pulp, unbleached and cooked cotton rag stock, semibleached and cooked cotton rag stock, bleached and cooked cotton rag stock, cooked bagasse fibers, cotton linter pulp of various types and grades, mechanical pulp both from coniferous and deciduous woods, cooked hemp, sisal, ramie, jute, carao, and other bast fiber stock such as bamboo, palm, and many grasses, old paper stock made up of any or all or any mixture of used papermaking fibers, cooked straw fibers, cooked flax fibers, and in fact any cellulosic fibrous material that lends itself to the formation of cellulosic webs or forms from its aqueous suspension.

Among the types of condensation polymers that are adaptable to the practice of the present invention are the following: phenol-formaldehyde resins, furfural-phenol condensation product; resorcinol-formaldehyde condensation products; urea-formaldehyde resins, melamine-formaldehyde resins, the reaction-condensation product of cyclohexanol, adipamide, adipic acid and hexamethylenedi-

amine, the trade name of which is "nylon"; the condensation-reaction product of phthalic anhydride, glycerol, and linoleic acid, the trade name of which is "Glyptal"; the condensation-reaction product of cyclopentadiene, maleic anhydride, glycerol, and linoleic acid, e. g. "Carbic" resin; the condensation-reaction product of dibasic acid, maleic anhydride, glycerol and styrene, e. g. "Laminac" resin; the condensation-reaction product of sebacic acid, ricinoleic acid and glycerol, e. g. "Paraplex" resin; the condensation-reaction product of sebacic acid and ethylene glycol, e. g. "paracon" resin; condensation-polymerization products of ethylene oxide or "Carbowax" resins; the condensation-reaction product of ethylene dichloride and sodium tetrasulfide, e. g. "Thiokol A" resin; and condensation-polymerization products of dimethyldichlorosilane or "silicone" resins.

Also, several types of varnish resins such as: parateritarybutylphenol formaldehyde resins; parateritarybutylureaformaldehyde resins; and parateritarybutylmelamine-formaldehyde resins are within the scope of the present invention.

Among the rosin (abietic acid) derivatives that are applicable to the process operation are the following: poly-pale rosin or polymerized rosin; esterified rosins in the form of pure rosin esters; glycerol esters of hydrogenated rosin; and the various grades of wood and gum rosins as normally used in the manufacture of sizing materials for the paper industry.

The vinyl type of polymers adaptable to the process operation may include the following: polyethylene; polystyrene; polydichlorostyrene; "Piccolyte" resins; coumarone-indene resins; polyisobutylene ("Vistanex") resins; methylmethacrylate; ethylmethacrylate; isobutylmethacrylate; butylmethacrylate; polyvinylacetate ("Vinylite"); polyvinylchloride ("Geon"); polyvinylbutylate; allyl alcohol copolymers ("Allymer CR" resins); and polyvinyl-formaldehyde ("Formvar"); etc.

Copolymeric types of plastics may include the following: vinylidene chloride plus acrylonitrile ("Saran"), vinyl chloride plus acrylonitrile ("Vinyon"); vinylchloride plus vinylacetate plus maleic anhydride ("maleic modified polyvinyl chloride acetate"); vinylidene chloride plus vinyl chloride ("Plioflex"); styrene plus drying oil ("Styrenated oil"), cyclo pentadiene plus drying oil ("cyclo oil").

Special technical resins that are applicable to process operation are various types of synthetic rubbers.

Synthetic rubbers may include the following: Butadiene plus styrene ("GR-S latex"), butadiene plus acrylonitrile ("GR-A latex"), isoprene plus isobutylene ("GR-I latex"), chloroprene polymerized product ("GR-M latex"), dimethyldichlorosilane polymerized product ("silicone rubber"), chlorohydrin plus formaldehyde plus sodium tetrasulfide ("organic polysulfide latex"). Other resins may include a class of resins known as hydrocarbon resins. Those are highly resinous materials of varying molecular weights and flow points and have a high utility value. Also included may be various types of asphalts, pitches, tars and the like.

The alkyd resins lend themselves to process operation and offer interesting possibilities in the production of new and unusual types of cellulose-alkyd resin-complexes. Among such resins finding application to quantitative combination with cellulosic fibers in aqueous suspension, by the methods of this invention, are: Pure alkyds of the drying type; phenolated alkyds, styrenated alkyds, rosin-modified alkyd resins, phthalic free alkyd resins.

The drying oils generally used to modify the alkyd resins are linseed, perilla, oiticica, fish, and tung oils; and in some alkyd resins use is made of soya bean oil, dehydrated castor oil, sunflower oil and walnut oil. The drying types of alkyd resins have a high degree of unsaturation due to their unsaturated fatty acid content, and due to the four double bonds in case of the fish oil fatty acids. Such alkyd resins may be combined in emulsified form with urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde and other types of plastic materials to give unusual products that impart a high utility value to the cellulose complexes that may be evolved by their use.

Natural latices are also adaptable to process operation, and natural rubber latex, and its modifications such as pre-vulcanized natural rubber latex, chlorinated natural rubber latex and other materials that are derived by modification of natural rubbers, are readily adaptable

to formulation into cationically reactive emulsions or dispersions, for use in the present process.

Natural gums and synthetic gums are readily formulated into cationically reactive emulsions or dispersions, and therefore are adaptable to process operation.

Plasticizing materials may be combined with the many water-insoluble materials, where a plasticizer is tolerated, and unusual filming properties thus added to the water-insoluble materials which generally, in the instance of plasticization, is of the plastic, resin, or elastomeric type of water-insoluble material.

There are many filling and loading materials that are readily adaptable to the operation of the process, as without exception they can be formulated into cationically reactive dispersions, and may include the following water-insoluble materials: asbestine, clays, bentonite, diatomaceous earths, gypsum, talc, basic lead carbonate, whiting, titanium oxide, natural barytes, lithophone, silica and others.

The waxes are all adaptable to the operation of the process: the natural waxes, the petroleum waxes, and the synthetic waxes in all their grades and types, as all are capable of being solvated and subsequently emulsified with an operable cationic emulsifier.

Oils are also amenable to the process, such as natural oils, e. g., vegetable oils, the mineral oils, and the synthetic oils, all being capable of solvation and subsequent emulsification into a suitable and operable cationically reactive emulsion. Such materials may serve to plasticize cellulose, and to impart unusual characteristics of high utility value to cellulosic webs and forms, and many new types of cellulose-oil complexes may be evolved.

There are a number of cellulose derivatives and modified celluloses that are likewise adaptable to the present process, such as: ethyl cellulose, carboxymethylcellulose, ethylcellulose, butyral cellulose, cellulose acetate, and others. Nitrocellulose, because of its highly combustible nature, is not indicated, although it is operable in the operation of the present process.

It is to be noted that other water-insoluble materials may prove to be of utility value in the production of a cellulose-water-insoluble-material complex web or form, and if such materials are adaptable to formulation into cationically reactive dispersions or emulsions they may be included in the practically unlimited list of water-insoluble materials adaptable to the present invention.

Other types of similar materials that may be included are: chlorinated paraffins; chlorinated rubbers; rubber hydrochloride; and many others.

There are many inorganic, organic and resinated pigment colors that are completely adaptable to this process of operation, and so offer many interesting possibilities in new methods of coloring cellulosic products. The following are suggested as representative of this class of materials: lead-sulfo-chromate; lead chromate; zinc chromate; "Hansa Yellow" (a primary aromatic amine coupled with aceto-acetanilid); basic lead chromate; lead-chrome molybdate; lead-chrome green; iron blue pigments; Prussian blue pigments; "Lithol reds" (the pigment produced by diazotizing 2-naphthylamine-1-sulfonic acid, coupling with beta-naphthol and salting out with either barium or calcium salts); resinated barium Lithol red; resinated calcium Lithol red; toluidine red (2-nitro-4-toluene-azo-beta-naphthol pigment dyestuff); para reds (similar to the toluidine reds); red lakes (barium salts of 1-naphthol-azo-2-oxynaphthalene-3:6 disulfonic acid); phthalocyanine blue. Targetoner red (an azo coupling of ortho-chloro-paranitraniline to beta naphthol); etc., all of which can readily be formulated to a cationically reactive dispersion, as was done in the instance of lead chromate (Example 7 hereinabove).

There are of course many other types of coloring materials that can readily be made into suitable cationically reactive dispersions for use in the process, such as: Bone black; carbon black; lamp black; ochre, umber, cobalt blue, mineral brown, red lead, iron yellow; cadmium red, Tuscan red, cadmium yellow, graphite, whiting, blanc fixe, and others. Metals such as comminuted aluminum, zinc, lead, etc., may also be used.

Preparation of cationically active emulsions for stage two of the present process

As the material that is to be deposited upon the cellulosic fibers must be in an emulsion or dispersion that exhibits cationic activity, and as the preparation of such

emulsions is of considerable importance in the present connection, there will now be given a number of examples of the preparation of such cationically active emulsions and dispersions. In order not to confuse the example numbers, these examples have been given designations of letters of the alphabet. Any of the subjoined formulas may be employed for the affixation of the particular additaments to the cellulosic fibers that have been conditioned by treatment with the various types of conditioning materials. It will be noticed that in most cases an organic liquid that itself exhibits surface-active properties is employed in the formulation of the emulsions or dispersions, usually as a solvent. The outstanding ingredient in these emulsions or dispersions is an 18-carbon atom amine salt, such as the acetate or hydrochloride. It appears that this type of amine salt is an essential and more or less critical part of the emulsions or dispersions, as in their absence the remarkably high degree of deposition of the additament is not obtained. Where hereinafter the "amine salt" is mentioned, it is intended as a shortened expression for the 18-carbon atom chain amine salt.

Emulsion A: Parts by weight

Methyl methacrylate resin	40
Toluene	60
18-carbon atom chain amine salt	2
Dissolve the above in the toluene and add to—	
Water	100
Homogenize thoroughly.	

Emulsion B:

Polypale rosin	60
Toluene	60
18-carbon atom chain amine salt	3
Dissolve the above in the toluene and add to—	
Water	180
Homogenize thoroughly.	

Emulsion C:

Hydrocarbon resin S-50	500
Toluene	750
Amine salt	25
Dissolve resin and the amine salt in the toluene and add to—	
Water	1259
Homogenize thoroughly.	

Emulsion D:

"Piccoumaron" S-115 resin	700
Xylene	300
Amine salt	35
Dissolve in the xylene and add to—	
Water	1000
Homogenize thoroughly.	

Emulsion E:

70% chlorinated paraffin	700
Xylene	300
18-carbon atom chain amine salt	35
Dissolve in the xylene and add to—	
Water	1000
Homogenize thoroughly:	

Emulsion F:

"P-190 Hydrogenated Ester Gum"	400
Xylene	100
Amine salt	20
Dissolve in the xylene and add to—	
Water	500
Homogenize thoroughly	

Emulsion G:

GR-I-70 rubber	330
Rubber solvent	710
Xylene	400
Amine salt	15
Dissolve above in the xylene and add to—	
Water	1000
Homogenize thoroughly.	

Emulsion H:

Polyethyl butyl methacrylate non-ionic dispersion	200
Amine salt	20
Homogenize in—	
Water	580

Emulsion I:

Paraffin wax 128° (melt wax)	200
Amine salt	40
Homogenize hot, at least heated to the melting point of the wax.	

Emulsion J:

Toluene-soluble vinyl resin	300
Toluene	700
Amine salt	40
Dissolve in the toluene and homogenize in—	
Water	1000

Emulsion K:

Polymerized rosin ester	45
Toluene	20
Amine salt	7
Homogenize in—	
Water	35

Emulsion L:

Polystyrene	150
Toluene	250
Amine salt	15
Homogenize in—	
Water	1000

Emulsion M:

Coumarone-indene resin	350
Toluene	150
Amine salt	35
Homogenize in—	
Water	965

Emulsion N:

Low molecular weight "Vistanex" (polyisobutylene)	500
Toluene	500
Amine salt	100
Homogenize in—	
Water	900

Emulsion O:

Pentaerythritol ester of rosin	250
Toluene	250
Amine salt	50
Homogenize in—	
Water	950

Emulsion P:

Hydrocarbon resin "S-5"	325
Toluene	325
Amine salt	100
Homogenize in—	
Water	900

Emulsion Q:

#2000 super "Beckacite" 18-gallon varnish with china-wood oil ¹	2000
Reduce to 50% N. V. solids with V. M. P. naphtha.	
Amine salt	55
Homogenize in—	
Water	1000

Emulsion R:

Phenol-formaldehyde resin	1000
Xylene	1000
Amine salt	55
Homogenize in—	
Water	1000

Emulsion S:

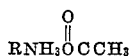
Neoprene GR-M latex	300
Xylene	700
Amine salt	15
Homogenize in—	
Water	1000

¹ A dielectric phenolic varnish.

The above examples of cationically active emulsions or dispersions are in addition to those previously mentioned in connection with the fourteen examples. In all cases the acetate of the 18-carbon chain amine has been used. Among the 18-carbon atom chain acids from which the amines are derived may be mentioned the following:

Octadecanoic acid (oleic acid); octadienoic acid (Vaccenic acid); octadecadienoic acid (linoleic acid). There are, of course, many other saturated and unsaturated 18-carbon atom chain fatty acids that may be used to advantage. It has been found that the octadecyl, octadecenyl and octadecadienyl amines that are most desirable for use

should have a mean molecular weight, of the primary amine content of the high molecular weight aliphatic amines, of within the range of from about 240 to 270, and the mean molecular combining weight of the primary amine should be in the range of from 270 to 320. To prepare the acetate of the amine of such a fatty acid, about 100 parts of the amine of octadecanoic acid may be treated with about 19.2 to 22.5 parts by weight of glacial acetic acid. In case of the octadienoic acid, about 19.4 to 22.2 parts of glacial acetic acid will be required. The glacial acetic acid should be added slowly to the amine at a temperature just above the melting point of the amine, say at about 55° to 75° C. Such an amine will have the formula of



These amine acetates are convertible into a substituted acetamide by the action of heat. This is an important fact, for it appears that the amine acetates are also deposited upon the cellulosic fibers. When the sheet or molded pulp object has been prepared, and heat is applied, as during drying or during the hot-pressing operation, the amine acetate is converted into a substituted acetamide. This serves to render the material deposited upon the cellulosic fiber irremovable by water, and greatly enhances the effect.

Further examples of the bonding of additaments to cellulosic fibers

To show the bonding of a heavy inorganic pigment to suspended cellulosic fibers in substantially quantitative proportions, the following example is given.

EXAMPLE 14

500 grams of unbleached southern kraft pulp were furnished to the laboratory beater and the stock well brushed for 30 minutes, after which, 40.00 grams of Alox L-1205-X¹, were added, and the beating operation continued for 1½ hours to develop a stock freeness of approximately 600 Canadian Green standard. At the end of the beating cycle a series of approximately 1% (bone-dry basis) treated fiber suspensions were made for a number of evaluations.

All of the cationically reactive dispersions and emulsions used were 2% nonvolatile solids dispersions or emulsions.

To one of the treated fiber suspensions were added 50 cc. increments of a 2% nonvolatile solids dispersion of titanium oxide (TiO₂); the pH value being taken on each addition, as below:

DATA

ccs. 2% N. V. Solids Dispersion TiO ₂ Added	pH Value after Addition	Condition of Liquid Phase
0.....	7.60	clear.
50.....	7.60	Do.
100.....	7.60	Do.
150.....	7.50	Do.

A hand sheet was made. There were no sticking tendencies evidenced at any point in processing. The white-water draining from the forming wire was crystal clear and free of visible particles. The sheet was dried to constant weight at 215° F.

A duplicate 1% fiber suspension was used to form a blank hand sheet, which was also dried to constant weight at 215° F. The results obtained were as follows:

Bone-dry weight titanium oxide solids added	grams--	3.00
Bone-dry weight blank hand sheet.....	do-----	13.64
Input total weight.....	do-----	16.64
Bone-dry weight processed sheet as above.....	do-----	16.86
Percentage of combination TiO ₂ with treated cellulose	per cent....	100

EXAMPLE 15

To another of the approximately 1% treated fiber suspensions from the beater stock of Example 14 were added, in 50 cc. increments, a cationically reactive 2% N. V.¹ solids dispersion of Hansa Yellow (a primary

¹ Abbreviation for "nonvolatile."

aromatic amine coupled with aceto-acetanilid—e. g., an organic pigment color) and the pH values taken after each addition as in the preceding examples.

DATA

cc. 2% N. V. Solids Cationically reactive dispersion Hansa Yellow added	pH Value after addition	Condition of liquid phase
0.....	7.90	clear.
50.....	7.70	Do.
100.....	7.60	Do.

A hand sheet was made. No sticking was in evidence at any point in processing. The white-water draining from the forming wire was crystal clear, and completely free from color. 20% solids organic pigment color had been added and the hand sheet was dried to constant weight at 215° F. The results were as follows:

Bone-dry weight solid Hansa Yellow pigment added	grams----	2.00
Bone-dry weight untreated hand sheet.....	do-----	13.64
Bone-dry weight processed hand sheet as above	grams--	15.60
Percentage of solid pigment color added	per cent....	20
Percentage of combination Hansa Yellow-treated cellulose	per cent....	98

EXAMPLE 16

500 grams of untreated, uncooked, raw cotton linters of the lowest grade were furnished to the laboratory beater, to the water of which had been added 5 grams of a nonionic surface active agent—Victawet M-12—in order that the raw cotton linters would be sufficiently wetted to permit beater circulation. Thereafter exactly 40 grams of "Alox L-1205-X" were added, and the cotton linters brushed for one hour to defiber the linter bundles. Thereafter the beater stock was dumped into a 20-gallon stoneware crock to permit an exact mixing and sampling—the stock agitated to a uniform suspension and the bone-dry consistency determined to be 2.16%. Thereafter exact 1% bone-dry treated cotton linter suspensions were made up for evaluation purposes. The liquid phase of the beater stock was noticeably dirty—the liquid being a blackish-gray in color.

To one of the 1% treated cotton linter suspensions were added successive 50 cc. increments of combined emulsions of cationically reactive emulsions as follows:

- (a) 50% polymerized esterified rosin
(b) 50% acrylonitrile-butadiene latex

DATA

cc. 2% N. V. solids combined cationically reactive emulsions—50%-50% (a) Polymerized esterified rosin (b) Acrylonitrile-butadiene latex	pH value after addition	Condition of liquid phase
0.....	7.10	dirty gray black liquid phase.
50.....	7.00	liquid phase noticeably lighter in color.
100.....	6.70	clear liquid.
150.....	6.70	Do.
200.....	6.50	Do.

Titration stopped at 200 cc., as this was end point desired. A hand sheet was made. There was no evidence of sticking at any point in the processing, and the stock was extremely free on the wire. An excellent sheet was produced, which was dried to constant weight at 215° F. The white-water was crystal clear. The results were:

Bone-dry composite resin solids added.....	Grams	4.00
Bone-dry weight blank hand sheet.....	do-----	8.75
Total input weight.....	do-----	12.75
Bone-dry weight processed sheet.....	do-----	13.95
Total input weight (based on blank hand sheet on sheet forming wire and consequent shrinkage loss)	do-----	12.75
Gain in weight over 100% combination of added resin solids.....	do-----	1.20
Loss in weight blank hand sheet from normal.....	do-----	1.25

The clearing of the liquid phase of the cotton linter suspension upon addition of the combined cationically reactive emulsions is significant and points to an almost complete pickup of the dirt solids in the liquid phase. This is explainable by the possible presence of excess cationic emulsifier in the cationically reactive emulsions added, in which case the dirt solids of the liquid phase would be swept into the cationically reactive emulsions and probably likewise given an electropositive charge—and hence would be combined with the treated cotton linters.

Percentage of combination added resin solids with cellulose	Per cent
Percentage of combination on retention, including the dirt solids	100
	96

The processed bone-dry sheet was cured at 800 p. s. i. and 320° F. for one minute. A tough, flexible, highly liquid-resistant sheet resulted, which had the feel and texture of leather.

EXAMPLE 17

A sample of pure cotton cellulose gauze, e. g., Johnson and Johnson sterilized surgical gauze, was obtained and used in these evaluations. Samples of the gauze were cut to 16" x 16" and bone dried to constant weight at 215° F. The average weight of the untreated gauze samples was 6.10 grams. A number of samples of gauze were immersed for approximately 5 minutes in a 5% solids dispersion of "Victamine C." Thereafter the samples to be used were removed, squeezed as dry as possible and immersed in a 2% solids dispersion of a series of cationically reactive resin emulsions for a period of approximately 5 minutes, and thereafter were thoroughly rinsed and washed several times with water, and thereafter stretched flat on an inclined board and thoroughly washed with a hose to completely remove all unbonded material. Thereafter the samples were dried to a constant weight at 215° F. The material used was a 2% N. V. solids cationically reactive emulsion of chlorinated paraffin. The results were as follows:

Bone-dry weight processed gauze	grams--	10.10
Bone-dry weight untreated gauze	do----	6.10
Chlorinated paraffin combined with cellulose	grams--	4.00
Per cent chlorinated paraffin combined	per cent by weight--	66

In a second test the following were used:

2% N. V. solids—cationically reactive emulsion of hydrogenated ester gum (polypale resin base)	
Bone-dry weight processed gauze	grams-- 11.17
Bone-dry weight untreated gauze	do---- 6.10
Hydrogenated ester gum combined with cellulose	grams-- 5.07
Per cent hydrogenated ester gum combined	per cent-- 83

EXAMPLE 18

A sample of pure cotton cellulose gauze, e. g., Johnson and Johnson sterile surgical gauze was weighed, and then immersed in a 2% active solids dispersion of "Victamine C" for several minutes. The sample was then squeezed as dry as possible to remove excess liquid and thereafter immersed in a 2% N. V. solids cationically reactive emulsion of polymethylmethacrylate for several minutes, washed with five wash waters and thereafter stretched flat on an inclined board and washed with a hose to remove all unbonded material. The gauze was then dried to constant weight at 215° F.

The results:

Bone-dry weight of processed gauze	grams--	10.42
Bone-dry weight of untreated sample	do----	5.63
Polymethylmethacrylate combined with gauze	grams--	4.79
Per cent polymethylmethacrylate combined	per cent by weight--	85

EXAMPLE 19

A piece of soft English chamois was obtained for evaluation. A piece of this leather material was weighed and thereafter immersed in a 2% active solids dispersion of "Victamine C" at 60° C. for a period of two

minutes. Thereafter the chamois was thoroughly squeezed to remove all excess liquid and then immersed in a 2% N. V. solids cationically reactive emulsion of polymethylmethacrylate for approximately two minutes, then rinsed and washed in six wash waters. Thereafter stretched flat on an inclined board, and well washed with a hose to remove all excess unbonded material. The processed leather was then dried to constant weight. The adsorption of the resin was remarkably high as shown by the results:

Bone-dry weight processed chamois leather	grams--	43.30
Bone-dry weight untreated chamois leather	grams--	18.60
Polymethylmethacrylate combined with leather	grams--	25.70
Percentage polymethylmethacrylate combined	per cent--	138

The processed leather was extremely tough and very flexible, and no resin was visible on the leather surface as such.

In order further to illustrate the wide range of materials that can be permanently affixed to cellulosic fibers by the processes of the present invention, and to demonstrate the conjoint use of "Victamine C" with a nonionic wetting agent such as "Victawet 12," which is useful in enabling the better wetting of the cellulosic material during the first stage of the process, the following additional examples are given.

EXAMPLE 20

300 grams (bone-dry basis) of low grade, untreated, uncooked, raw cotton linters and 200 grams (bone-dry basis) of unbleached southern kraft pulp were furnished to the laboratory beater, to the water of which had been added ½ of 1% of "Victawet 12" (a nonionic surface active agent) to permit an effective wetting of the cotton linters. After brushing out the fibers for one-half hour, 1% of "Victamine C" was added (based on bone-dry fiber weight), the addition being made in the form of a 15% aqueous dispersion. The beating was continued for 1½ hours, after which the bone-dry beater consistency was determined and a series of 1% (bone-dry basis) treated fiber suspensions made up for evaluation.

A 2% N. V. solids cationically reactive emulsion of "Pentalyn K" (a high melting point pentaerythritol ester of rosin) was made up for evaluation in electrometric titrations of the standard 1% (bone-dry basis) treated fiber suspensions (1,000 grams total suspension weight). 50 cc. increments thereof were added at a time and the pH values determined on each addition.

DATA

cc. 2% N. V. solids cationically reactive emulsion of high melting point pentaerythritol ester of rosin added	pH values after addition	Comments on liquid phase
0	7.60	clear.
50	6.70	instant pickup—clear.
100	6.40	Do.
150	6.10	Do.
200	5.90	Do.
250	5.70	Do.
300	5.65	Do.
350	5.55	Do.
400	5.50	Do.
450 (XX)	5.60	liquid phase white hazy.
500 (XX)	5.65	liquid phase white opaque.

To a duplicate 1% treated fiber suspension 400 cc. of the above 2% N. V. solids cationically reactive emulsion were added, and, after reaction, a hand sheet made therefrom. The liquid phase was crystal clear, as was also the white-water. A blank hand sheet was made for quantitative evaluation from the duplicate unprocessed suspension. The results were as follows:

Bone-dry weight "Pentalyn K" solids	grams--	8.00
Bone-dry weight blank hand sheet	do----	9.37
Bone-dry weight processed hand sheet	do----	17.85
Per cent combination "Pentalyn K" processed fiber	per cent--	100

During the titration, at the points marked "XX" on the above table, there were great fluctuations and oscillations in the indicator needle during the electrometric titration,

which indicates a high degree of unstable electronic conditions in the liquid phase. Unless noted by "XX," no fluctuation or oscillation of the indicator needle took place. This symbol (XX) will be used hereinafter in all electrometric titration data, to indicate the above-detailed unstable electronic conditions, and when used will denote the above conditions. The pH value of the 2% N. V. solids cationically reactive emulsion of "Pentalyn-K" was 5.20.

EXAMPLE 21

To one of the standard 1% (bone-dry basis) treated fiber suspensions from the beater stock of Example 20, 50 cc. increments of a 2% N. V. solids cationically reactive emulsion of polyisobutylene were added, the pH value being determined at each addition.

DATA

cc. 2% N. V. solids cationically reactive emulsion of polyisobutylene added	pH value after addition	Comments on liquid phase
0.....	7.70	clear.
50.....	7.20	instant pickup—clear.
100.....	7.00	Do.
150.....	6.75	Do.
200.....	6.60	Do.
250.....	6.45	Do.
300.....	6.40	Do.
350.....	6.30	Do.
400 (XX).....	6.20	white cloudy liquid phase.
450 (XX).....	6.25	white opaque liquid phase.
500 (XX).....	6.40	Do.

The pH value of the 2% N. V. solids cationically reactive emulsion of polyisobutylene was 5.20.

To a duplicate 1% treated fiber suspension of the treated beater stock of Example 20, 350 cc. of the above 2% N. V. solids cationically reactive emulsion were added, and after the reaction, a hand sheet was made therefrom and the sheet dried to constant weight at 215° F. During the formation of the sheet the liquid phase and white water were crystal clear, and there was no sticking at any point in the processing. An excellent sheet was produced, which was cured at 310° F. and 800 p. s. i. for 2 minutes. The results were as follows:

Bone-dry weight polyisobutylene solids—grams— 7.00
 Bone-dry weight blank hand sheet—do— 9.37
 Bone-dry weight processed hand sheet—do— 18.01
 Per cent combination of polyisobutylene treated fiber —————per cent— 100

EXAMPLE 22

To one of the standard 1% treated fiber suspensions prepared from the treated beater stock of Example 20, 50 cc. increments of a 2% N. V. solids cationically reactive emulsion of polystyrene resin were added, the pH value being determined at each addition.

DATA

cc. 2% N. V. solids cationically reactive emulsion of polystyrene resin added	pH value after addition	Comments on liquid phase
0.....	7.20	clear.
50.....	6.95	instant pickup—clear.
100.....	6.85	Do.
150.....	6.50	Do.
200.....	6.35	Do.
250.....	6.20	Do.
300.....	6.10	Do.
350.....	6.00	Do.
400.....	5.80	Do.
450 (XX).....	5.60	liquid phase, white hazy.
500 (XX).....	5.50	liquid phase, white opaque.
550 (XX).....	5.50	Do.
600 (XX).....	5.50	Do.

The pH value of the 2% N. V. solids cationically reactive emulsion of polystyrene resin was 5.50.

To a duplicate 1% treated fiber suspension, there were added 350 cc. of a 2% N. V. solids cationically reactive emulsion of polystyrene resin and, after the reaction, a hand sheet made therefrom. The liquid phase and white water were crystal clear, and there was no sticking at any

point. The sheet was dried to constant weight at 215° F. The results were as follows:

Bone-dry weight polystyrene resin solids—grams— 7.00
 Bone-dry weight blank hand sheet—do— 9.37
 Bone-dry weight processed hand sheet—do— 16.81
 Per cent combination of polystyrene resin solids with treated cellulose fibers was 100%.

A series of further examples, e. g., 23, 24, 25, 26, and 27, are the result of evaluation studies in the production of resin-cellulose complexes, designed to serve as replacement material for asphalt saturated felts, such as now used in the manufacture of floor coverings. The primary objectives were to produce base materials of approximately 0.055" caliper; 350# bias weight 24" x 36"—480# (finished); which, upon curing at 310°–320° F. and at a pressure of 800 p. s. i. for 5 minutes, would result in a tough, rubber-like, flexible, liquid-resistant material, suitable for use as a replacement of the present materials. The total resin-solids content was desired to be approximately 40% of the fiber weight. All of the examples employ two types of resins in the resin component of the complex material, the resins being selected for reasons of their indicated properties. All of the base materials produced in this series of examples exceeded all the desired specifications—all were acceptable for use. All were flowed or cured under the conditions as detailed hereinabove, and in no instance was there any evidence of flash, bleeding, or extrusion of the resin content, even though all samples were pulled hot, i. e., at 310°–320° F., which normally cannot be done with either thermally plastic or elastomeric types of resins. This is most unique to the present process. Although no platen lubricant was used (such as stearic acid), there was no evidence of sticking to the hot platens (310°–320° F.) when pulled hot, which is abnormal for the materials used. All evidence on conversion definitely points to a primary bonding of resin to cellulose. With the exception of the resin complexes used, the procedure was identical throughout this series (Examples 24–28, inclusive). 14" x 14" hand sheets made for sample purposes, and 6½" x 6½" sheets made for curing cycle evaluations. The details as to these examples are as follows:

EXAMPLE 23

To a standard 1% treated fiber suspension (stock of Example 20) 50 cc. increments of a 2% N. V. solids cationically reactive combination emulsion were added and the pH values determined. The combination cationically reactive emulsion used consisted, in this case, of equal parts (solids basis) of:

- (a) A pentaerythritol ester of rosin, and
 (b) An acrylonitrilebutadiene copolymer elastomer

DATA

cc. 2% N. V. solids cationically reactive combination emulsion as above added	pH value after addition	Comments on liquid phase
0.....	7.50	clear.
50.....	7.10	instant pickup—clear.
100.....	6.85	Do.
150.....	6.70	Do.
200 (40% resin).....	6.70	Do.

The pH value of 2% N. V. solids cationically reactive combination emulsion as above used was 5.80. A hand sheet was made at the end of the titration cycle. The white water was crystal clear, and no sticking was evidenced at any point. The sheet was bone dried at 215° F. The results were:

Bone-dry resin combination solids added—grams— 4.00
 Bone-dry weight hand sheet (blank)—do— 9.37
 Bone-dry weight processed hand sheet—do— 13.74
 Per cent combination—resin solids—treated fiber —————per cent— 100

Sheet composition:

- 60 parts raw cotton linters
 40 parts unbleached kraft pulp
 20 parts pentaerythritol rosin ester
 20 parts acrylonitrile-butadiene elastomer

This produced an excellent cured product, which was extremely tough, flexible, and resistant to penetration by liquids.

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EXAMPLE 24

To a standard 1% treated fiber suspension (stock of Example 20) 50 cc. increments of a 2% N. V. solids cationically reactive combination resin emulsion were added, pH values being taken at each addition. The combination resin emulsion consisted of equal parts (solids basis) of:

- (a) Pentaerythritol rosin ester, and
(b) Polyisobutylene ("Vistanex" rubber)

DATA

cc. 2% N. V. solids combination cationically reactive emulsion as above added	pH value after addition	Comments on liquid phase
0.....	8.10	clear.
50.....	7.50	instant pickup—clear.
100.....	7.10	Do.
150.....	7.10	Do.
200 (40% resin).....	7.00	Do.

The pH value of 2% N. V. solids resin combination emulsion as above was 6.20. A hand sheet was made at the end of the titration cycle. The white water was crystal clear, and there were no sticking tendencies. The sheet was bone dried at 215° F. The results were:

Bone-dry weight resin solids added.....grams--	4.00
Bone-dry weight blank hand sheet.....do-----	9.37
Bone-dry weight processed hand sheet.....do-----	13.38
Per cent combination, resin solids treated fiber.....per cent--	100

Sheet composition:

- 60 parts raw cotton linters
40 parts unbleached kraft pulp
20 parts pentaerythritol ester of rosin
20 parts polyisobutylene ("Vistanex")

It produced an excellent cured product, which was tough, flexible, and waterproof, and which did not show the slightest evidence of sticking to hot platens (310°–320° F.) when pulled hot.

EXAMPLE 25

To a standard 1% treated fiber suspension (stock of Example 21) 50 cc. increments of a 2% N. V. solids cationically reactive combination resin emulsion were added, pH values being taken at each addition. The combination resin emulsion consisted of equal parts (solids basis) of:

- (a) Pentaerythritol ester of rosin, and
(b) Hydrocarbon resin (modified rubber "S-5")

DATA

cc. 2% N. V. solids combination cationically reactive emulsion added as above	pH value after addition	Comments on liquid phase
0.....	7.60	clear.
50.....	6.90	instant pickup—clear.
100.....	6.70	Do.
150.....	6.50	Do.
200 (40% resin).....	6.25	Do.

The pH value of 2% N. V. solids cationically reactive resin combination emulsion as above was 5.30. Hand sheets were made at the end of the titration cycle. The white water was crystal clear, and there was no sticking. The sheet was bone dried at 215° F. The results were:

Bone-dry weight resin solids added.....grams--	4.00
Bone-dry weight blank hand sheet.....do-----	9.37
Bone-dry weight processed hand sheet.....do-----	13.90
Percent combination resin solids treated fiber.....per cent--	100

An excellent cured product, which was tough, flexible, and waterproof, resulted. It had the following composition:

- 60 parts raw cotton linters
40 parts unbleached kraft pulp
20 parts pentaerythritol ester of rosin
20 parts hydrocarbon resin (modified rubber "S-5")

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EXAMPLE 26

To a standard 1% treated fiber suspension (stock of Example 20) 50 cc. increments of a 2% N. V. solids cationically reactive combination resin emulsion were added, pH values being taken at each addition. The combination resin emulsion consisted of equal parts (solids basis) of:

- (a) Pentaerythritol ester of rosin, and
(b) Polyethylbutyl-methacrylate resin

DATA

cc. 2% N. V. solids combination cationically reactive emulsion added above	pH value after addition	Comment on liquid phase
0.....	7.55	clear.
50.....	7.00	instant pickup—clear.
100.....	6.70	Do.
150.....	6.55	Do.
200 (40% resin).....	6.55	Do.

The pH value of the 2% N. V. solids resin combination emulsion as above was 5.20. A hand sheet was made at the end of titration cycle, and the white water was crystal clear, and there was no sticking. The sheet was bone dried at 215° F. The results were:

Bone-dry weight resin solids added.....grams--	4.00
Bone-dry weight blank hand sheet.....do-----	9.37
Bone-dry weight processed hand sheet.....do-----	14.03
Percent combination resin solids treated fiber.....per cent--	100

This formed an excellent cured product which was extremely tough and rawhide-like in feel, very flexible, and waterproof. It had the following composition:

- 60 parts raw cotton linters
40 parts unbleached kraft pulp
20 parts pentaerythritol ester of rosin
20 parts polyethylbutyl-methacrylate resin

EXAMPLE 27

To a standard 1% treated fiber suspension (treated stock of Example 20) 50 cc. increments of a 2% N. V. solids cationically reactive resin combination emulsion were added, pH values being taken at each addition. The combination resin emulsion consisted of equal parts (solids basis) of:

- (a) Polyisobutylene ("Vistanex"), and
(b) Polyethylbutyl-methacrylate resin

DATA

cc. 2% N. V. solids combination cationically reactive emulsion added above	pH value after addition	Comments on liquid phase
0.....	7.50	clear.
50.....	7.25	instant pickup—clear.
100.....	7.10	Do.
150.....	6.90	Do.
200 (40% resin).....	6.90	Do.

The pH value of the 2% N. V. solids resin combination emulsion as above was 5.40. A hand sheet was made at the end of the titration cycle, and the white water was crystal clear, and there was no sticking. The sheet was bone dried at 215° F. The results were:

Bone-dry weight resin solids added.....grams--	4.00
Bone-dry weight blank hand sheet.....do-----	9.37
Bone-dry weight processed hand sheet.....do-----	13.38
Percent combination resin solids treated fiber.....per cent--	100

This formed an excellent cured product with peculiar properties, very, very tough and yet very flexible, and a 0.055" cured sheet was impossible to tear by hand. It was resistant to hot and cold water for hours and ap-

peared translucent, with apparently no grain visible. The sheet composition was as follows:

60 parts raw cotton linters
40 parts unbleached kraft pulp
20 parts polyisobutylene ("Vistanex")
20 parts polyethylbutyl-methacrylate resin

EXAMPLE 28

A very striking example of the complete compatibility of resins in cationically reactive emulsions, which normally are not compatible, and a striking example also of the tremendous flexibility of the present process in affording an infinite number of complexes of cellulosic fibers with noncellulosic materials, in endless possible combinations, is as follows:

A standard 1% treated fiber suspension (as in Example 20) was electrometrically titrated with a combined cationically reactive resin emulsion which consisted of equal parts each of the following resinous materials, all cationically reactive:

- (a) Polyisobutylene ("Vistanex" rubber)
- (b) Pentaerythritol ester of rosin ("Pentalyn K")
- (c) Hydrocarbon resin "S-5" (modified rubber)
- (d) Polyvinylchloride resin
- (e) Coumarone-indene resin
- (f) Polyethylbutyl-methacrylate resin

DATA

cc. 2% N.V. solids cationically reactive complex resin emulsion as detailed above	pH value after addition	Comments on liquid phase
0	7.40	clear.
50	7.15	instant pickup—clear.
100	7.15	Do.
150	7.15	Do.
200 (40% resin)	7.15	Do.

The pH value of the above 2% N. V. solids complex resin emulsion as above was 6.20. A hand sheet was made at the end of the titration cycle. The liquid phase and white water were clear, and there was no sticking at any point. A peculiar but excellent sheet resulted, showing great uniformity of formation and having a leathery feel and appearance. The hand sheet was dried to constant weight at 215° F. The results were as follows:

Bone-dry weight resin solids added-----grams-- 4.00
Bone-dry weight blank hand sheet-----do----- 9.85
Bone-dry weight processed hand sheet-----do----- 13.80
Percent combination resin solids treated fibers per cent-- 100

The composition of the sheet thus made is:

60 parts raw cotton linters
40 parts unbleached kraft pulp
6.66 parts polyisobutylene
6.66 parts pentaerythritol ester of rosin
6.66 parts hydrocarbon resin S-5
6.66 parts polyvinylchloride
6.66 parts coumarone-indene resin
6.66 parts polyethylbutyl-methacrylate resin

This sheet was cured at 310°-320° F. at 800# p. s. i. for 5 minutes. A tough, highly glazed, leatherlike product resulted, impervious to penetration with water over a long period, difficult to tear, and very pliable—a peculiar combination of physical characteristics.

Special aspects of the invention

In the development of suitable cationically active dispersions or emulsions of the additaments by the aid of the salt of the 18 carbon atom chain fatty acid amines, it was found that the type of organic solvent employed to form the disperse phase was important, and that the hydrocarbons that gave satisfactory results were aromatics rather than aliphatics. Thus, toluene and xylene were found to be eminently satisfactory, while petroleum types of solvents were inoperative, even when used conjointly with an aromatic such as toluene or xylene. Benzene is counterindicated, mainly because of its low boiling point and the resulting fire hazard because of its volatility, and possibility of the formation of explosive mixtures. Also, benzene is quite toxic, while toluene and xylene are com-

paratively innocuous. In place of the pure aromatic hydrocarbons, coal tar oils may be used, as these contain toluene, xylene and their higher homologues.

There will now be described an example (29) which has some very outstanding characteristics, in that there were noticed, in connection with the operations, rather striking phenomena, namely, the formation of clusters or rope-like agglomerations of the cellulose fibers and the additament, so that it would appear as though at least a sort of physical "co-polymerization" or "condensation" had taken place. Thus, while the suspension of the cellulose fiber after treatment with the conditioning reagent and the emulsion of the additament were both murky and almost opaque, yet as soon as the two suspensions were added to each other there would be an almost instantaneous physical reaction by which large, and in some cases star-like, and in other cases, rope-like, agglomerations would form, leaving the liquid otherwise clear. These agglomerations would persist in spite of the most vigorous agitation, showing a very strong attachment of the additament to the fiber.

EXAMPLE 29

To one of the standard 1% treated fiber suspensions as prepared with "Victawet 12" and "Victamine C," as already described, 50 cc. increments of a 2% N. V. solids cationically reactive combined resin emulsion, consisting of 2 parts of polyethylbutyl-methacrylate and 1 part of pentaerythritol ester of rosin, were added, and the pH value determined at each addition. This combined resin emulsion is a combination of large molecules, and complicated molecules, as will be understood. In this titration the above-mentioned phenomenon of complex fiber clusters appeared. The clusters formed at a fixed pH value, and during their formation there was observed a great lack of electronic stability, as will be noted. At the end of the titration, the liquid phase, although initially white and cloudy, and with a widely fluctuating indicator needle, cleared in from 1 to 2 minutes, and the indicator needle dampened down to a fixed reading as the liquid phase cleared.

The formation of this example could be termed a cluster rather than a rope but nevertheless a definite agglomeration or complex configuration of the complex fibers took place.

This phenomenon could well be related to what might, for lack of established nomenclature, be termed an—

(a) "Emulsion polymerization," if the cellulose fiber suspension could be considered an "emulsion of cellulose"; or

(b) "Suspension polymerization," if the cellulose fiber suspension could be regarded as a "suspended monomer"; but—

(c) It most probably is "Polar polymerization" of which little is known and nothing as yet published. If such can be considered the case, then cellulose in an activated condition as treated with a cationically reactive surface-active conditioning agent, could be considered as a "catalytic cationic monomer" in a chain addition type of polymerization where electron availability for promoting such chain addition polymerization will come from the numerous double bonds in the reacting cationically active solids phase of the long chain, large molecular sized, resin additaments as it has been noted that the formation of "complex fiber clusters or ropes" (which definitely appear to be products of chain addition polymerization) takes place mostly with long chain, highly complex, large molecular sized resins.

There is all reasonable basis to establish this phenomenon as a "cationic polymerization" of:

(a) Cationically activated cellulosic structure containing double bonds; and a

(b) Cationically activated complex long chained, large molecular size non-cellulosic materials containing double bonds.

The southern unbleached kraft pulp used in these tests had a very high lignin content and, therefore, was high in "double bonds." It is well known that a simple double bond has a pair of electrons readily available for the promotion of addition reactions. There is thus a basis for this theory of "cationic polymerization." The process could, therefore, quite aptly be described as one of polar polymerization of cationically reactive complex "mono-

mers," each or all of which contain a multiplicity of double bonds and a high degree of electron availability.

EVALUATION DATA OF EXAMPLE 29

cc. 2% N. V. Solids Combined Cationically Reactive Emulsion of 2 parts Polyethylbutylmethacrylate and 1 part pentaerythritol ester of rosin	pH Value after Addition	Comments on Liquid Phase
0.....	7.60	clear.
50.....	6.80	instant pick up—clear.
100.....	6.50	Do.
150.....	6.25	Do.
200 (40% added).....	6.10	Do.
250.....	5.90	Do.
300.....	5.85	Do.
350 "clusters".....	5.75	Do.
400 (XX) "clusters" form.....	5.60	Do.
450 (XX) "clusters" form.....	5.60	Do.
500 (XX) "clusters" form.....	5.60	Do.
550 (XX) "clusters" form.....	5.60	slow adsorption—cloudy.
600 (XX) "clusters" form.....	5.60	cloudy—clear 1 minute.
650 (XX) "clusters" form.....	5.60	cloudy—clear 2 minutes.
700 (XX) "clusters" form.....	5.60	Do.

¹ Note lack of change in hydrogen-ion concentration.

The pH value 2% N. V. solids combined emulsion as used above was 4.75 pH.

To an exact duplicate 1% treated fiber suspension, as immediately above, 200 cc. of the above cationically reactive combined resin emulsion was added, with agitation, and after reaction, hand sheet made and dried to constant weight at 215° F.

The liquid phase and white-water were clear, and there was no sticking evidenced at any point. A very tough, leatherlike sheet, when cured at 310° F. at 800 p. s. i. for three minutes resulted. The results, as to the product, were:

Bone-dry weight resin solids added.....	grams--	4.00
Bone-dry weight blank hand sheet.....	do.....	9.90
Bone-dry weight processed hand sheet.....	do.....	13.95
Percent combination resin solids—treated fiber	percent..	100

EXAMPLE 30

To a 1% (bone dry basis) "Alox" treated fiber suspension, weighing 1,000 grams, 50 cc. increments of a cationically reactive emulsion consisting of equal parts of polyethylbutylmethacrylate and paratertiarybutylphenol-formaldehyde resin were added and the pH value determined at each addition.

EVALUATION DATA

cc. 2% N. V. Solids Cationically Reactive Emulsion Consisting of 1 part Paratertiary-butylphenolformaldehyde and 1 part Polyethylbutyl - methacrylate added	pH Value after Addition	Comments on Liquid Phase
0.....	6.80	clear.
50.....	5.80	instant pickup—clear.
100.....	5.40	Do.
150.....	5.20	Do.
200 (XX) "ropes" form.....	5.00	Do.
250 (XX) "ropes" form.....	5.00	Do.
300 (XX) "ropes" form.....	5.00	Do.
350 (XX) "ropes" form.....	5.00	Do.
400 (XX) "ropes" form.....	5.00	Do.
450 (XX) "ropes" form.....	5.00	Do.
500 (XX) "ropes" form.....	5.00	Do.

A series of 14" x 14" hand sheets were made corresponding to the end of the above titration cycle, although the end point of the resin-cellulose combination had not been reached. These sheets are among the most striking examples of the process operation of the present invention. The liquid phase was crystal clear, as was also the white water. There was no sticking at any point. Fiber-resin ropes were apparent in the sheet which dried normally, and was calendered, and cured at 310° F., and 900 lbs. p. s. i. for two minutes. There was extremely uniform resin flow. The sheet was highly grease and water resistant.

The actual composition of this sheet was:

50% unbleached kraft pulp
25% paratertiary-butylphenolformaldehyde resin
25% polyethylbutylmethacrylate

EXAMPLE 31

A cationically reactive emulsion of butyl rubber was used—made up to a 2% N. V. solids emulsion. A standard 10 grams of 1% Alox treated fiber suspension was electrometrically titrated with the above emulsion.

EVALUATION DATA

cc. 2% N. V. Solids Cationically Reactive Emulsion of Butyl Rubber Added	pH Value after Addition	Comments on Liquid Phase
0.....	7.40	clear.
50.....	6.60	instant pickup—clear.
100.....	6.30	Do.
150.....	6.10	Do.
200 (XX) "ropes" form.....	6.00	Do.
250 (XX) "ropes" form.....	5.95	Do.
300 (XX) "ropes" form.....	5.90	Do.

A series of 60 grams (bone dry fiber base) 14" x 14" hand sheets were made by adding to a 1% treated fiber suspension containing 60 grams of bone dry treated fiber, 1,800 cc. of a 2% N. V. solids cationically reactive emulsion of butyl rubber. The liquid phase and white water were clear, and the retention was completely quantitative. Excellent sheets resulted which were dried normally, and then calendered and embossed. Actual sheet composition:

62.5% unbleached southern kraft pulp
37.5% butyl rubber

The rope-like fibers were very apparent in the sheets, the formation being very open, and appearing like interlocked ropes.

EXAMPLE 32

500 grams (bone dry basis) Brunswick full bleached kraft pulp were furnished to the laboratory beater, and after brushing for one-half hour, 30 grams (as is) of "Alox L-1205-X" were added, and the beating continued for one and one-half hours. Thereafter the bone dry beater consistency was determined to be 1.61%, and, on this basis, a series of exactly 1% treated fiber dispersions were made up, each being 1000 grams total weight.

To one of these portions of the thus treated beater stock there was added, in 25 cc. increments, a 2% N. V. solids cationically reactive emulsion of Lithol Red (a pigment produced by diazotizing 2-naphthylamine-1-sulfonic acid; coupling with beta-naphthol and salting out with a barium salt, and classified as a "resinated organic pigment"), a total of 125 cc. being added, the liquid phase remaining crystal clear and free from color throughout the addition. A hand sheet was made. No sticking was evidenced. The white water was crystal clear and free from color. The sheet was dried to constant weight at 215° F. The sheet was brilliant scarlet in color, and no trace of two sidedness was evident. The ultimate results were:

Bone-dry weight Lithol Red solids added.....	grams--	2.50
Bone-dry weight hand sheet blank.....	do.....	10.42
Bone-dry weight processed sheet.....	do.....	13.05
Percentage Lithol Red solids added.....	per cent..	25
Percentage Lithol Red solids combined with fiber	per cent..	100

EXAMPLE 33

A supply of soft English chamois was secured and samples cut therefrom and weighed. Samples were immersed in a 2% N. V. solids dispersion of "Victamine C" for several minutes and thereafter squeezed dry to remove excess liquid, and immersed in a 0.50% cationically reactive dispersion of an organic type pigment for several minutes at room temperature (approximately 75° F.), the pigment used being known as "Hansa Yellow."

Thereafter, the colored leather samples were taken from the cationically reactive dispersion, washed until no trace of color appeared in the wash water, stretched flat on an inclined board and washed with a hose to remove all unbonded materials, and thereafter dried to a constant weight at 215° F.

The results were—

	Grams
Bone-dry weight processed leather.....	31.05
Bone-dry weight untreated leather.....	22.80
85% "Hansa Yellow" color solids.	

29

Percentage "Hansa Yellow" solids combined—36%. This is a remarkably high retention for leather.

EXAMPLE 34

To demonstrate the ease with which uniformly colored products could be made by the use of water-insoluble coloring matter, standard 10-gram treated fiber suspension, treated with 6% Alox L-1205-X' and beaten as usual, was electrometrically titrated with a 0.50% N. V. solids of a cationically reactive dispersion of Phthalocyanine Blue. The primary objective of this evaluation was to determine the rapidity of reaction, as showing possibilities of coloring paper products by the addition of cationically reactive dispersions of pigment dyestuffs to a machine head box, to eliminate by so doing the washing up of beaters and stock chests that normally takes place with color changes. Such a method of coloring paper would, therefore, be of great benefit as related to the production of colored papers. Overall operating costs would be considerably reduced by such a procedure.

The Phthalocyanine Blue is a coordinated copper complex of tetra-azo-tetra-benzo-porphin and has a complicated structural formula, being essentially a chelate compound.

Phthalocyanine pigments are insoluble in water and substantially insoluble in the vehicles and solvents used commercially in the pigment-consuming industries. They may be dissolved in strong acids, e. g., sulfuric, from which they are precipitated in the original chemical form upon dilution. Their resistance to chemical agencies, e. g., oxidation and reduction, is unusual. They are essentially unreactive.

EVALUATION DATA OF EXAMPLE 34

cc. 0.50% N. V. Solids Cationically Reactive Dispersion of Phthalocyanine Blue Added	pH Value after Addition	Comments on Liquid Phase
0.....	7.50	clear.
5.....	7.65	instant pick-up—clear.
10.....	7.65	Do.
15 (XX) violent oscillation.....	7.65	Do.
20 (XX) violent oscillation.....	7.65	Do.
25 (XX) violent oscillation.....	7.65	Do.
30 (XX) violent oscillation.....	7.65	Do.
35 oscillation stopped.....	7.50	Do.
40.....	7.50	Do.
45.....	7.50	Do.
50.....	7.45	Do.
55.....	7.45	Do.
60.....	7.45	Do.
65.....	7.45	Do.
70.....	7.45	Do.
75.....	7.45	Do.
80.....	7.45	Do.
85 (XX) slight oscillation.....	7.40	Do.
90 (XX) slight oscillation.....	7.35	Do.
95 (XX) slight oscillation.....	7.35	Do.
100 (XX) visual end.....	7.30	slight bluish tint in liquid phase that disappeared in 1 minute.

A hand sheet was made at the end of the titration cycle. The liquid phase was colorless, as was the white water. There were no sticking tendencies, nor bleeding on white blotters used to couch the sheet, which was dried to constant weight at 215° F.

HAND SHEET DATA

Bone-dry weight of Phthalocyanine Blue solids added.....	grams.....	0.500
Bone-dry weight of blank hand sheet.....	do.....	9.168
Bone dry weight processed sheet as above.....	do.....	9.672
Per cent actual Phthalocyanine Blue in sheet.....	per cent.....	5.04
Per cent actual retention Phthalocyanine blue.....	per cent.....	100

Demonstration of variations in conditioning agents

In the further examples to be given, the additament selected was always an acrylonitrile-butadiene copolymer elastomer, the only variations being in the conditioning material used during the first step. The emulsion of such copolymer was always one that exhibited pronounced cationic properties, i. e., the particles in suspension had a positive charge. Therefore, the further examples are strictly comparable as to results, and serve as illustrations of the breadth of scope of that portion of the present in-

30

vention which relates primarily to the conditioning of the material upon which the additaments are deposited.

EXAMPLE 35

5 The Victor Chemical Works, Chicago, Illinois, produced in their research laboratory a "Victamine analog" using an unsaturated acid (B-6518) which is an 18 carbon atom chain acid. This analog is a white waxy solid which is difficult to disperse in water, but is readily soluble in toluene.

10 A 5% N. V. solids aqueous dispersion of this material was made up at 80° C., and used in this evaluation work. It was necessary to maintain the temperature at 80° C., to insure the stability of the dispersion, as with a drop in temperature of 15 to 20° C., the waxy solid separated from the aqueous phase and floated on the surface.

15 A standard 1,000 gram, exact 1% untreated fiber solid suspension was electrometrically titrated with a 5% N. V. solids aqueous dispersion of this Victamine analog (unsaturated acid B-6518). The electrometric titration is most interesting and extremely unusual. It is noted that no foaming and no oscillation took place at any point on the titration cycle.

EVALUATION DATA

cc. 5% N. V. Solids Aqueous Dispersions of Victamine Analog Added to Untreated Pulp	pH Value after Addition	Comments on Liquid Phase
0.....	8.00	clear.
1.....	8.00	Do.
2.....	8.00	Do.
3.....	8.00	Do.
4.....	8.05	Do.
5.....	8.05	Do.
6.....	8.10	Do.
7.....	8.10	Do.
8.....	8.10	Do.
9.....	8.15	Do.
10.....	8.15	Do.
11.....	8.20	Do.
12.....	8.20	Do.
13.....	8.20	Do.
14.....	8.20	Do.
15.....	8.20	Do.
16.....	8.20	Do.
17.....	8.20	Do.
18.....	8.20	Do.
19.....	8.20	Do.
20.....	8.20	Do.
21.....	8.25	Do.
22.....	8.25	Do.
23.....	8.25	Do.
24.....	8.25	Do.
25.....	8.25	Do.

40 4 cc. of 5% N. V. solids aqueous dispersion of Victamine analog (unsaturated acid B-6518) were added to a standard 1,000 gram exact 1% untreated fiber solid dispersion and the mixture agitated for 15 minutes. Thereafter, the mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of the acrylonitrilebutadiene copolymer.

EVALUATION DATA

cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene Added to Treated Pulp	pH Value after Addition	Comments on Liquid Phase
0.....	8.00	clear.
50.....	7.75	slow adsorption—cleared.
100.....	7.60	Do.
150.....	7.50	Do.
200.....	7.40	Do.
250.....	7.35	slow adsorption—cleared 40 s.
300.....	7.30	Do.
350 (XX) ropes.....	7.25	Do.
400 (XX) ropes.....	7.20	Do.
450 (XX) ropes.....	7.15	slow adsorption—cleared 60 s.
500 (XX) ropes.....	7.15	Do.

75 Results: Hand sheet made at end of titration cycle; liquid phase clear; white water clear; a very noticeable rope-like formation in the sheet; no sticking or foaming tendencies; sheet dried at constant weight of 215° F.

80 Bone-dry weight of blank hand sheet.....	grams.....	9.60
Bone-dry weight of processed hand sheet (avg.).....	grams.....	19.94
Per cent acrylonitrilebutadiene solids in sheet.....	per cent.....	100
85 Per cent retention added solids.....	do.....	100

The processed sheet in the wet state was extremely light colored, and noticeably showed the rope-like fibers. The reaction between the treated fibers and the cationic reactive plastic emulsion was noticeably slow, as is noted above.

EXAMPLE 36

Evaluation of "Sapamine KWC."—"Sapamine KWC" is a cationically reactive surface-active agent, and is properly described as being a compound in which a "hydrophobic group is joined to the cationic group through an amide intermediate linkage." "Sapamine KWC" is made under United States Patents 1,737,458, 2,186,464, 2,329,406, and 2,357,598, and is a quaternary ammonium salt of an analog of diethylaminoethylolethylamidehydroacetate. It is a cocoa brown powder, insoluble in water at normal temperatures, and forms a brownish colored viscous dispersion in water at 212° F. A 2½% aqueous dispersion of "Sapamine KWC," at 212° F., was prepared for evaluation, and the temperature of the dispersion maintained at this point as it was found that a decrease in temperature resulted in breaking the dispersion. Fluctuations were evident during the titration, details of which are here omitted to shorten the specification.

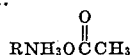
8 cc. of 2½% N. V. solids aqueous dispersion of "Sapamine KWC" were added to a standard 1000 gram 1% untreated fiber solids suspension and the mixture agitated for fifteen minutes. Thereafter, the mixture was electrometrically titrated with a 2% N. V. solids cationic reactive emulsion of acrylonitrilebutadiene. There was a very pronounced formation of rope-like aggregations.

A hand sheet was made at the end of titration cycle, which showed a very noticeable rope formation, but no sticking or foaming tendencies. The white water was cloudy. The sheet was dried to constant weight at 215° F. Results:

Bone-dry weight of blank hand sheet	grams	9.60
Bone-dry weight of processed sheet	do	18.90
Per cent acrylonitrilebutadiene solids in sheet		
	per cent	93
Per cent retention resin solids	do	93

EXAMPLE 37

Evaluation of "Armac 18-D."—"Armac 18-D" is a high molecular weight aliphatic amine acetate, having the structural formula:



where R is an 18 carbon atom aliphatic chain, and constitutes the hydrophobic group. It is water-insoluble and disperses with difficulty to a thick viscous dispersion of 2½% N. V. solids concentration. It was considered advisable to evaluate this material for the reason that it is extremely cationically reactive, and further has a multiplicity of unsaturated linkages in the fatty acid hydrophobic group. Accordingly, a 2½% N. V. solids aqueous dispersion of Armac 18-D was prepared for evaluation, and also because it is a material useful in step II of the present invention, i. e., for preparing cationically active emulsions or suspensions.

8 cc. of a 2½% N. V. solids aqueous dispersion of "Armac 18-D" were added to 1,000 gram 1% untreated fiber solids suspension and the mixture agitated for fifteen minutes. Thereafter the mixture was electrometrically titrated with a 2% N. V. solids cationic reactive emulsion of acrylonitrilebutadiene. The evaluation data are omitted, but it may be stated that "rope formation" was highly in evidence.

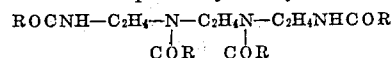
The reaction between the treated fibers and the cationic reactive resin emulsion was extremely slow, and from the first addition of cationically reactive acrylonitrilebutadiene emulsion, very pronounced rope-like fibers formed, which formation continued throughout the titration. For reason of the uniqueness of this reaction it was decided to carry the reaction through to clear liquid phases regardless of the time element. At the end of the titration cycle foam developed in the mixture and the stock floated on the top of the liquid phase. A hand sheet was made after the liquid phase was clear (5 to 10 minutes). Very pronounced rope-like fibers were evident in the sheet, particularly in the wet stage before pressing. There was no sticking on

the wire, but a slight sticking tendency on the felts. The sheet was dried to a constant weight at 215° F. Results:

Bone-dry weight of blank hand sheet	grams	9.90
Bone-dry weight processed hand sheet	do	20.00
Per cent acrylonitrilebutadiene solids in sheet		
	per cent	100
Per cent retention added resin solids	do	100

EXAMPLES 38A and 38B

This is an evaluation of a new type of cationic reactive surface active agent, e. g., a crude reaction product resulting from condensing one mol of triethylenetetramine with four mols of naphthenic acid having an acid number of 210. The resultant product has an acid number of approximately 30, indicating the presence of a small amount of unreacted naphthenic acid and some incompletely reacted amine. The product may be technically termed tetranaphthenoyltriethylenetetramine, i. e.,



and can be classified as that type of cationic reactive surface active agent in which the basic hydrophilic group is linked in a heterocyclic ring.

The material can further be classified as an imidazoline, e. g., the reaction product of the condensation reaction of polyethylene polyamines with long chain acids, i. e. naphthenic acid, and more specifically could be defined as an aminoethylimidazoline.

This material is a very high viscosity oil—dark in color, insoluble in water, but soluble in a variety of organic solvents, e. g. toluol and methanol.

It was found impossible to formulate a good aqueous dispersion of the material, and accordingly two solutions were prepared for evaluation work: a 5% N. V. solids solution of aminoethylimidazoline in toluene as used in Example 38A and a 5% N. V. solids solution of aminoethylimidazoline in methanol as used in Example 38B. Both solutions were brown-black in color, and free from any visible suspended particles. The laboratory beater was furnished with unbleached southern kraft pulp and the stock beaten to a condition closely duplicating the beater stock as used in foregoing evaluations. Thereafter the bone-dry consistency was determined and a series of 1,000 gram exact 1% (bone-dry basis) untreated fiber solids suspensions prepared for evaluations and hand sheet production.

Four cc. of a 5% N. V. solids toluene solution of the tetranaphthenoyltriethylenetetramine were added to a 1,000 gram, 1% untreated fiber solids suspension and the mixture agitated for 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene. A hand sheet was made at the end of titration cycle. The liquid phase had cleared and the white water was clear. There were no sticking tendencies at any point in the processing. The hand sheet was O. K. and was dried to constant weight at 215° F.

A series of untreated fiber suspensions of 1,000 grams each were made into blank hand sheets; the sheets dried to a constant weight at 215° F. and the average bone-dry weight of the blank hand sheets determined.

Bone-dry weight blank hand sheet	grams	9.60
Bone-dry weight processed hand sheet above		
	grams	13.93
Bone-dry weight blank hand sheet above	do	9.60
Per cent resin solids in sheet	per cent	40
Per cent retention added resin solids	do	100

EXAMPLE 39

A 1,000 gram, 1% untreated fiber solids suspension (bone-dry basis) was electrometrically titrated with a 5% N. V. solids aqueous dispersion of a naphthenoyl amide salt, the dispersion being a cloudy, grayish brown-black suspension of finely divided particles. It is the diacylated (acetate) salt of naphthenoyltetramide.

Four cc. of a 5% N. V. solids aqueous dispersion of the naphthenoyl amide salt M153.1 were added to 1000 grams of a 1% untreated fiber solids suspension (bone-dry basis) and the mixture agitated 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

33

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene added to above treated fibers	pH Value after Addition	Comments on Liquid Phase
0.....	7.75	clear.
50.....	7.60	instant pickup—clear.
100.....	7.50	slower pickup—clear.
150.....	7.50	slower pickup—clear 1 min.
200.....	7.45	Do.
250.....	7.45	slower pickup—clear 2 mins.

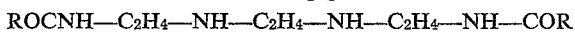
Hand sheet made at end of titration cycle. Liquid phase clear. White water clear. No sticking tendencies. Hand sheet O. K. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet.....grams.... 14.67
 Bone-dry weight blank hand sheet.....do..... 9.63
 Per cent resin solids in sheet.....per cent.... 50
 Per cent retention added resin solids.....do..... 100

The "naphthenoylamide salt M153.1" is a water-insoluble, very high viscosity, dark brown-black oil.

EXAMPLES 40A AND 40B

This covers the evaluation of a new type of surface active agent, naphthenoylpolyamide M152, considered to be a polyamide derived from the reaction product of the condensation of naphthenic acid with a polyethylene-polyamine. "Naphthenoylpolyamide M152" is a high viscosity oil, dark brown-black in color, and is water-insoluble. It has the following general formula:



It is dispersible in water with difficulty, and aqueous dispersions prepared are not stable and readily break, necessitating constant agitation to keep the oil particles in a good suspension. It is, however, soluble in a variety of organic solvents, including toluene. The aqueous dispersions prepared are brown-black in color and unstable. A 5% N. V. solids aqueous dispersion of the naphthenoylpolyamide M152 was prepared for evaluation. It was quite unstable, requiring constant agitation during titration additions, being brown-black in color. A 5% N. V. solids toluene solution of it was also prepared for evaluation. This was clear and deep brown-black in color.

The untreated beater stock as used in Example 38A was used in the evaluations of Example 40A and the untreated beater stock as used in Example 38B was used in the evaluations of Example 40B. The naphthenoylpolyamide M152 is at present manufactured as a pilot plant product by the Dearborn Chemical Company of Chicago, Illinois, and is considered to be an ampholytic surface active agent, having both basic and acidic groups in the same molecule.

EXAMPLE 40A

A 1000 gram, 1% untreated fiber solids suspension (bone-dry basis) as used in Example 38A was electrometrically titrated with a 5% N. V. solids toluene solution of "naphthenoylpolyamide M152." The pH increased and reached 10.00. For testing, 4 cc. of a 5% N. V. solids toluene solution of this polyamide were added to 1000 grams of a 1% untreated fiber solids suspension (bone-dry basis) and the mixture agitated 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene added to above treated fibers	pH Value after Addition	Comments on Liquid Phase
0.....	9.15	clear.
50.....	9.00	instant pickup—clear.
100.....	8.90	Do.
150.....	8.85	Do.
200.....	8.75	Do.
250.....	8.50	slower pickup—clear.
300 (visual end).....	8.50	very slow pickup—clear 3 min.
350.....	8.40	cloudy white.

34

Hand sheet made at end of titration cycle. Liquid phase hazy white, water hazy. No sticking tendencies at any point. Hand sheet O. K. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet.....grams.... 15.86
 Bone-dry weight blank hand sheet.....do..... 9.60
 Per cent resin solids in sheet.....per cent.... 63
 Per cent retention added resin solids.....do..... 90

EXAMPLE 40B

A 1000 gram, exact 1% untreated fiber solids suspension (bone-dry basis) as used in Example 38B was electrometrically titrated with a 5% N. V. solids aqueous dispersion of naphthenoylpolyamide M152. The titration proceeded smoothly, the pH gradually increasing to 10.15. There was no foaming at any point and the solution remained clear.

Thereafter 4 cc. of a 5% N. V. solids aqueous dispersion of naphthenoylpolyamide M152 were added to 1000 grams of a 1% untreated fiber solids suspension (bone-dry basis) and the mixture agitated for 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene Added to Above Treated Fibers	pH Value after Addition	Comments on Liquid Phase
0.....	8.80	clear.
50.....	8.75	instant pickup—clear.
100.....	8.65	Do.
150.....	8.55	slower pickup—clear.
200.....	8.40	Do.
250.....	8.30	Do.
300.....	8.20	Do.
350.....	8.10	slower pickup—slight haze 1 min.

Hand sheet made at end of titration cycle. No sticking tendencies at any point. Very, very slight haze in liquid phase and white water. Hand sheet O. K. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet.....grams.... 16.50
 Bone-dry weight blank hand sheet.....do..... 9.63
 Per cent resin solids in sheet.....per cent.... 69
 Per cent retention added resin solids approximately.....do..... 100

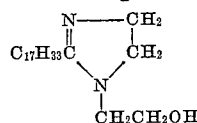
From this example it will be seen that the aqueous dispersion of naphthenoylpolyamide M152 is more effective in process reactions than is the toluene solution of this material.

EXAMPLE 41

In this example, the conditioning agent was of a type in which a basic hydrophilic group is linked in a heterocyclic ring. Accordingly a sulfonated alkyl benzimidazole was used in the form of a 5% N. V. S. aqueous dispersion, as the material is substantially insoluble in water but forms a dirty gray, highly turbid suspension. Thus to a 1% untreated fiber suspension 4 cc. of such an emulsion were added and, after agitating the suspension for 15 minutes, it was titrated with a 2% N. V. S. cationically reactive emulsion of an acrylonitrile-butadiene copolymer. Rope formation was noted early in the process and the pH of the suspension dropped from 7.65 to 7.15. The pick-up was perfect and amounted to 100%.

EXAMPLE 42

The material used in this example is "Amine 220," technically termed: 1-hydroxyethyl-2-heptadecenyl-glyoxalidine and has the following structural formula:



Its molecular weight is 350 and the equivalent weight is 175. The boiling point is 235° C. Viscosity at 100° F. equals 150 centipoises. It is soluble in mineral and

vegetable oils, in common organic solvents and is very slightly soluble in water, but for all practical purposes it is insoluble in water. The commercial product as obtained contains 80% of the cyclic glyoxalidine, the balance being the linear amide of oleic acid and aminoethylethanolamine. Aqueous dispersions of Amine 220 are alkaline, though the material is highly cationically reactive.

A 5% N. V. solids aqueous dispersion of Amine 220 was prepared with difficulty—it being found necessary to heat the Amine 220 water mixture to about 195° F.—and to pass the heated mixture through a colloid mill three to four times to effect a smooth suspension that remained stable only at elevated temperatures, and rapidly became unstable as the temperature of the dispersion decreased to approximately room temperature, necessitating the maintenance of an elevated temperature of approximately 190° F. of the Amine 220 aqueous dispersion during the titration cycles. The dispersion so made was light, creamy and translucent.

A 1000 gram, 1% untreated fiber solids suspension (bone-dry basis) was electrometrically titrated with a 5% N. V. solids aqueous dispersion of Amine 220, it being noted that the pH increased from 8.10 to 9.15.

An exact duplicate 1000 gram, 1% untreated fiber solids (bone-dry basis) suspension was treated by adding thereto 4 cc. of the 5% N. V. solids aqueous dispersion of Amine 220, and the mixture agitated for 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

EVALUATION DATA

Ccs. 2% N. V. Solids Cationic Emulsion of Acrylonitrile-butadiene added to Amine 220 Treated Fibers	pH Value after Addition	Comments on Liquid Phase
0.....	8.60	clear.
50 ropes.....	8.35	instant pickup—clear.
100 ropes.....	8.20	Do.
150 ropes.....	8.05	Do.
200 ropes.....	7.80	slower pickup—cleared.
250 ropes.....	7.80	Do.
300 ropes.....	7.80	Do.
350 ropes ¹	7.80	very much slower pickup—cleared 3 min.
400 ropes.....	7.80	Do.
450 ropes.....	7.80	Do.
500 ropes.....	7.80	Do.

¹ Note the peculiar titration, and the very slow reaction at end. An extremely tough hand sheet resulted. Liquid phase clear. White water clear. No sticking tendencies at any point in processing. Excellent tough sheets resulted. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet..... grams... 19.80
Bone-dry weight blank hand sheet..... do..... 9.78

"Pickup"..... do..... 10.02

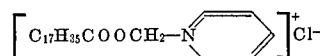
Percent resin solids in sheet..... percent... 100
Percent retention added resin solids..... do..... 100

Amine 220 is made by condensing oleic acid with 2-aminoethylethanolamine at above 150° C., and xylene is used to remove the water of reaction as fast as it forms. A second terminology for Amine 220 is hydroxyethylimidazoline and it belongs to the class of cationically reactive agents in which the basic hydrophilic group is linked in a heterocyclic ring. United States patents covering the manufacture of this material are: 2,267,965, 2,268,273, 2,355,837, 2,200,815 and 549,328 (British).

EXAMPLE 43

A special type of cationically reactive material, Norane R, was used in this example. It is "Norane R," manufactured under United States Patents 2,261,097, 2,282,948, 2,315,135 and 2,386,631. It is not described technically by the manufacturer, but is said to be made (according to the patent disclosures) by the combination of stearic acid chloride, formaldehyde and pyridine. It is a soft, tan-colored paste, insoluble in water, and extremely difficult to disperse. A 5% N. V. solids aqueous dispersion of Norane R was prepared by beating the Norane R water mixture to about 200° F., and passing the heated mixture through a colloid mill several times. A light cream-colored dispersion resulted of poor stability—necessitating the continual agitation of the dispersion during

titration cycles. The stability remains satisfactory at 200° F., but decreases as temperature of dispersion decreases to room temperature. The general structural formula of Norane R is:



To a 1000 gram, 1% untreated fiber solids (bone-dry basis) suspension 4 cc. of a 5% N. V. solids aqueous dispersion of Norane R were added and the mixture agitated 15 minutes. Thereafter, the reacted mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

A hand sheet made at end of titration cycle. Liquid phase clear. White water clear. No sticking tendencies at any point. Excellent sheet. Sheet dried to constant weight at 215° F. A very, very tough sheet resulted.

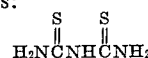
Bone-dry weight processed hand sheet..... grams... 19.95
Bone-dry weight blank hand sheet..... do..... 9.78

"Pickup"..... do..... 10.17

Percent resin solids in sheet..... percent... 100
Percent retention resin solids..... do..... 100

EXAMPLE 44

Dithiobiuret is an "off white" colored crystalline solid, having a melting point of 193–195° C. It is a strong reducing agent, nearly completely insoluble in cold water. Very slightly soluble in hot water and is classified as water dispersible. Soluble in dioxane, pyridine, aqueous caustic solution, acetone, Cellosolve and ethanol. Its structural formula is as follows:



Laboratory beater was furnished with unbleached southern kraft pulp, and stock beaten to a condition closely approximating the stock condition of previous evaluation runs. Thereafter, bone-dry beater consistency determined, and a series of exact 1000 gram, exact 1% fiber solids suspensions (bone-dry basis) prepared for evaluations and hand sheet data. Bone-dry beater consistency—1.61%.

To a 1000 gram, 1% untreated fiber solids suspension (bone-dry basis) 4 cc. of a 5% N. V. solids aqueous dispersion of dithiobiuret were added, the mixture agitated for 15 minutes, and thereafter electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

The usual tests were made. During the addition of the acrylonitrilebutadiene emulsion the pH of the fiber suspension dropped from 8.00 to 7.60, and the pick-up was good. Sixty per cent of resin solids were incorporated in the sheet and the retention was 100%.

EXAMPLE 45

Diallylcyanamid is a water-insoluble product—a clear mobile liquid having a boiling point of 153° C., and a melting point of –70° C. It is very soluble in most organic solvents. It dissolves many synthetic and natural resins. It has possible uses as an intermediate inorganic syntheses and as a solvent, and has the structural formula detailed below:



A 5% N. V. solids methyl ethyl ketone solution of diallylcyanamid was prepared for use in evaluations and hand sheet production. The pH value of this solution was 7.55.

To a 1000 gram, 1% untreated solids suspension 4 cc. of a 5% N. V. solids methyl ethyl ketone solution of diallylcyanamid were added, the mixture agitated for 15 minutes and thereafter electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene. "Ropes" formed right at the start of the titration and the pick-up was clear.

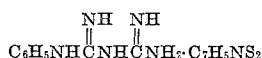
Hand sheet made at end of titration cycle. Liquid phase clear. White water clear. No sticking tendencies at any point in processing. Sheet dried to constant weight at 215° F. Excellent sheet, clear and uniform.

Bone-dry weight processed hand sheet..... grams... 19.90
Bone-dry weight blank hand sheet..... do..... 9.91
Per cent resin solids in sheet..... per cent... 100
Per cent retention added resin solids..... do..... 100

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EXAMPLE 46

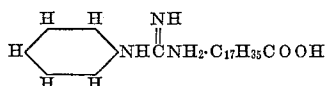
In this example, the conditioning agent was phenylbiguanide MBT salt, the letters "MBT" standing for mercaptobenzothiazole, the formula for which is given as



It is a crystalline solid having a melting point of 171° C., is substantially insoluble in water and alcohol, but soluble in acetone. The tests on this substance were therefore conducted with a 5% N. V. S. solution in acetone. The usual procedure, hereinabove outlined, was used, 4 cc. of the acetone solution being added to 1000 grams of a 1% fiber suspension, which was subsequently, after the usual 15 minutes agitation, treated with a 2% N. V. S. emulsion of acrylonitrilebutadiene. Rope formation was quite prominent. The pick-up of the added material was 100%.

EXAMPLE 47

Phenylguanidinate is a water-insoluble, cream-colored crystalline solid that softens at 60° C. The pH of a saturated aqueous dispersion equals 8.5 pH. It is dispersible in warm water and very soluble in alcohol and benzene. The structural formula for phenylguanidine-stearate is:



A 5% N. V. solids aqueous dispersion of phenylguanidinate was prepared for use in this evaluation, the pH value of which was 10.05.

To a 1000 gram, 1% untreated fiber solids suspension 4 cc. of a 5% N. V. solids aqueous dispersion of phenylguanidinate were added, the mixture agitated 15 minutes, and thereafter electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene, as standard practice. Rope formation was very marked.

Hand sheet made at end of titration cycle. Liquid phase clear. White water clear. No sticking tendencies at any point. Excellent sheet clear and well formed. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet-----grams-- 20.07
Bone-dry weight blank hand sheet-----do----- 9.91
Per cent resin solids in sheet-----per cent----- 100
Per cent resin solids added-----do----- 100
Per cent retention resin solids-----do----- 100

EXAMPLE 48

This example represents the addition of neoprene to kraft fibers. Using the techniques already described, the conditioning agent employed was phenylbiguanidehydrochloride and the additament was neoprene in the form of a 2% N. V. S. cationically active emulsion. Enough of the latter was added to amount to 40% addition. The pick-up was perfect and amounted to 100%.

EXAMPLE 49

Rosin Amine D is a water-insoluble primary amine of high molecular weight derived from rosin acids. It is a pale yellow, viscous liquid having a density of 0.997 at 25° C. It is soluble in most organic solvents, but practically insoluble in water. It readily forms salts with mineral acids and with organic acids of low molecular weight. The bromine number of Rosin Amine D is 49. The flash point is 192° C. The nitrogen content is from 4.3% to 4.5%.

To a 1000 gram, 1% untreated fiber solids suspension 4 cc. of a 5% N. V. solids methyl ethyl ketone solution of Rosin Amine D were added, the mixture agitated 15 minutes, and thereafter electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene, as hereinabove outlined as a standard evaluating procedure. As in other examples, the pick-up was 100% and no difficulties were encountered.

Addition of metal powders

One of the remarkable features of the present invention is the possibility of introducing relatively large amounts of metal powders into a paper sheet or pulp product. It would hardly be expectable that such electrically conducting substances as zinc powder, aluminum powder and the like would be operative from a cation-

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ically reactive suspension, but it nevertheless proved to be a fact, as is witnessed by the following examples. When these are combined with an elastomer such as a synthetic rubber, for example an acrylonitrile-butadiene copolymer, sheets eminently suitable for making gaskets are obtained.

EXAMPLE 50

The laboratory beater was furnished with unbleached southern kraft pulp and after brushing out the fibers for one-half hour, exactly 6% as is basis of Alox L-1205-X' was added and the beating continued for one hour. Thereafter the bone dry consistency was determined and a series of exact 1% bone dry basis treated fiber suspensions prepared for electrometric evaluations and hand sheet production.

1000 grams of a standard, 1% bone dry basis treated fiber suspension (equivalent to 10 grams fiber solids) was electrometrically titrated with a 5% N. V. solids cationically reactive dispersion of metallic aluminum.

EVALUATION DATA

Cc. 5% N. V. Solids Cationically Reactive Dispersion of Aluminum Added	pH Value After Addition	Comments on Liquid Phase
0.....	7.60	clear.
25.....	6.90	instant pickup—clear.
50.....	6.30	Do.
75.....	6.10	Do.
100.....	6.10	Do.
125.....	6.10	Do.
150.....	6.10	Do.
175.....	6.10	Do.
200.....	6.10	Do.

pH value of 5% N. V. solids dispersion metallic aluminum=5.90.

Hand sheet made at end of titration cycle. Liquid phase clear. White water clear. Stock very slow on wire. No sticking tendencies at any point. No metallic deposit on white blotters. Extremely fantastic sheet produced, with silvery metallic sheen. Completely metallized appearance throughout sheet. Hand sheet dried to constant weight at 215° F. and weight recorded.

HAND SHEET DATA

Bone dry weight metallic aluminum added-----grams-- 10.00
Bone dry weight blank hand sheet-----do----- 10.03
Bone dry weight processed hand sheet-----do----- 20.38
Actual metallic aluminum in sheet-----per cent----- 100.0
Retention metallic aluminum added-----do----- 100.0

This is without doubt the most spectacular example to date—for reason of the silvery metallic appearance of the sheet, which would be more spectacular with a clean, fully bleached fiber base. It is a striking example of metallized cellulose, and the example indicates industrial possibilities in making "metallized paper" for a variety of uses, such as gaskets etc.

EXAMPLE 51

The usual beater stock was used in this evaluation, having been treated with Alox. A cationically reactive dispersion of zinc dust was prepared for use in this example.

A standard 10-gram Alox-treated fiber suspension (exact 1% bone dry fiber solids) was electrometrically titrated with a 2% N. V. solids cationically reactive dispersion of metallic zinc.

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Dispersion of Metallic Zinc Added	pH Value After Addition	Comments Liquid Phase
0.....	8.25	clear.
50.....	8.00	instant pickup—clear.
100.....	7.70	Do.
150.....	7.50	Do.
200.....	7.40	Do.
250.....	7.40	Do.
300.....	7.40	Do.
350.....	7.40	Do.
400.....	7.50	slower adsorption—gray hazy.
450.....	7.60	slow adsorption—gray cloudy.
500.....	7.65	gray cloudy liquid.

A hand sheet made from an exact duplicate 1% treated fiber suspension—after reacting it with 350 cc. (70% metallic zinc) of a 2% N. V. solids cationically reactive dispersion of metallic zinc. Instant pick up. Liquid

phase clear. White water clear. Excellent gray-brown sheet made. Dried sheet to constant weight at 215° F.

HAND SHEET DATA

Bone dry weight metallic zinc added-----grams--	7.00
Bone dry weight blank hand sheet-----do-----	10.86
Bone dry weight processed hand sheet-----do-----	18.10
Actual metallic zinc in sheet-----per cent-----	70
Retention of added metallic zinc solids-----do-----	100

Actual sheet composition:

59% unbleached kraft pulp
41% metallic zinc

Pressed at 1000 p. s. i. and 370° F. for 6 minutes, a strip of the zinc-cellulose-complex acquired a metal-smooth glazed surface.

EXAMPLE 52

The treated beater stock of Example 50 was used in this evaluation. Previous electrometric titrations were used as a basis of additions.

A series of 14" x 14" hand sheets were made of 30-gram bone dry treated fiber base, using a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene and a 5% N. V. solids cationically reactive dispersion of metallic aluminum.

Liquid phase clear. Instantaneous reaction. White waters clear. No sticking tendencies at any point in processing. Spectacular appearing hand sheet resulted. No metallic bleeding on white blotters used to couch and press sheet. Sheets dried normally and calendered. On drying sheets assumed a silvery sheen, which was accentuated on calendering.

Actual sheet composition:

50% unbleached kraft pulp
25% metallic aluminum
25% acrylonitrilebutadiene

A strip of the sheet was cured at 320° F. at 800 p. s. i. and 20 minutes. Cured strip had silvery metallic lustre and was tough and flexible.

Powdered minerals

Another important feature of the present invention is the fact that it enables the introduction into paper and pulp products of quite unusually high filler contents, such as calcium carbonate (an alkaline filler), diatomaceous earth and other forms of silica, and similar substances that lend specific properties to the paper or pulp products. While ordinarily it is not possible to introduce more than about 20% by weight of such fillers into paper or pulp, the present invention makes it quite feasible to introduce 100% or even more, which is totally unexpected and entirely novel. The following examples are illustrative of such processes.

EXAMPLE 53

The primary objectives of this example were:

To formulate a cationically reactive dispersion of calcium carbonate of fine particle size, to evaluate the control factors governing the incorporation or combination of such a cationically reactive dispersion of calcium carbonate with treated cellulose; and to evaluate the resultant product of such combination as a flame resistant material, and also as a calcium carbonate filled sheet, which would have a high utility value in itself, regardless of its flame-resistant properties. It was considered that the selection of "Atomite" a highly developed calcium carbonate pigment was a logical selection based on the physical and chemical properties of this material as detailed below.

Average mean particle size-----microns--	2.5
Hardness -----	3.0
pH -----	9.2-9.5
Specific gravity -----	2.71
Water-soluble salts -----per cent--	0.07

Chemical composition:

CaCO ₃ -----per cent--	98.20
MgCO ₃ -----do-----	1.20
Al ₂ O ₃ -----do-----	0.12
SiO ₂ -----do-----	0.45
Fe ₂ O ₃ -----do-----	0.06
MnO -----do-----	0.01
Moisture -----do-----	0.20

This "Atomite" contains practically no water-soluble salts, shows no adsorbed or occluded ions, and is not hygroscopic.

(A) 300 grams of "Atomite" dispersed in 1000 grams of water containing 10 grams of Victawet 12, a non-ionic surface active agent which was added to the water to insure a complete wetting of the calcium carbonate particles.

(B) 60 grams 18 carbon atom chain amine acetate dissolved in 1630 grams of water at 60° C. (A) added to (B) through colloid mill, making several passes through mill to secure complete homogenization and smooth dispersion of N. V. solids. Water added to make suspension equal to 10% solids content.

A laboratory beater was furnished with unbleached kraft pulp, and after brushing the stock for one-half hour, exactly 6% "as is" Alox L-1205-X' was added and the beating continued for one hour. Thereafter the bone-dry consistency was determined and a series of exact 1% treated fiber suspensions prepared (bone-dry basis) for electrometric evaluations and hand sheet manufacture.

A series of exact 1% bone-dry treated fiber suspensions, each weighing 1,000 grams, were used to make blank hand sheets. These hand sheets were dried to constant weight at 215° F. and the bone-dry weight established.

Average bone-dry weight blank hand sheet—10.20 grams.

A standard 10-gram, 1% treated fiber suspension (bone-dry basis) was electrometrically titrated with a 2% N. V. solids cationically reactive dispersion of "Atomite" (calcium carbonate).

EVALUATION DATA

Co. 2% N. V. Solids Cationically Reactive Dispersion of Atomite (Calcium Carbonate) added	pH Value After Addition	Comments on Liquid Phase
35 0-----	7.55	clear.
50-----	7.80	instant pickup—clear.
100-----	7.95	Do.
150-----	8.10	Do.
200-----	8.10	Do.
250 (end point)-----	8.10	Do.
300-----	8.15	cloudy liquid phase.
40 350-----	8.20	Do.

This is a peculiar electrometric titration, showing a sharp break point. Hand sheet made of exact duplicate fiber suspension plus 250 cc. above dispersion. Liquid phase clear. White water clear. Sheet O. K. Dried hand sheet to constant weight at 215° F.

HAND SHEET DATA

Bone-dry weight calcium carbonate added-----grams--	5.00
Bone-dry weight blank hand sheet-----do-----	10.20
Bone-dry weight processes hand sheet-----do-----	15.31
Actual calcium carbonate solids in sheet-----per cent--	50
55 Retention of added calcium carbonate solids-----per cent--	100

Actual sheet composition:

66.66% unbleached kraft pulp
33.33% calcium carbonate

EXAMPLE 54

The treated beater stock of Example 53 was used in this evaluation. A cationically reactive dispersion of diatomaceous silica, e. g., "Dicalite BP-4-5" was prepared for evaluation. A 10-gram standard treated fiber suspension, 1% bone-dry treated fiber solids suspension was electrometrically titrated with a 2% N. V. solids cationically reactive dispersion of diatomaceous silica, which latter is the fossil remains of tiny marine plants called diatoms. Other terminology for this material includes the following: Infusorial earth, diatomaceous earth, kieselguhr diatomite, amorphous silica, Celite and Dicalite. The material is both chemically and physically inert and contains no adsorbed or occluded ions. The principal use thereof heretofore in paper making has been that of a bulking agent—dispersing agent for asphalt, pitch, etc. Large percentages of diatomaceous silica incorporated or combined with cellulose may produce a unique material. The greatest amount of such material that has been used commercially in paper is about 20% (on the fiber weight) and in this instance, in excess of 50% (on the fiber weight) was added in order to retain 20% diatomaceous silica solids in the sheet, the normal retention by precipitation being very low.

Using the already familiar technique, a hand sheet

made at the end of the titration cycle. Liquid phase clear. White water clear. No sticking tendencies observed. Excellent sheet. Sheet dried to constant weight at 215° F. and weight recorded.

A blank hand sheet made from an exact duplicate 1% treated fiber suspension. Sheet likewise dried to constant weight at 215° F. and weight recorded.

HAND SHEET DATA

Bone-dry weight diatomaceous silica added	grams--	10.00
Bone-dry weight blank hand sheet-----do-----		10.86
Bone-dry weight processed hand sheet-----do-----		20.90
Per cent diatomaceous silica solids in sheet	per cent--	100
Per cent retention of added diatomaceous silica solids -----per cent--		100

Other examples

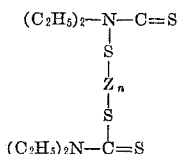
It has also been found feasible to introduce not only the additament, but also modifying agents therefor, such as accelerators and plasticizers, so that these could act upon the additament during the subsequent operations. Thus, and also within the scope of this particular phase of the present invention, two mutually reactive or mutually influencing additaments may be formed into a cationically active emulsion and the latter then allowed to act upon the fibers. This also contemplates the utilization of certain conditioners which, in addition to conditioning the fibers for the subsequent acceptance of the additament also impart certain desirable qualities to the fiber product produced or acted upon, such as rendering it water-repellent, fire- and flame-resistant, etc. This may include imparting toxic, fungicidal, and insect- and rodent-repelling materials into the fiber content.

EXAMPLE 55

To demonstrate the joint effect of an additament and a modifying agent therefor, an esterified tall oil (AVO 3480) and ethyl zimate (a drying accelerator) were made up into a cationically reactive emulsion as follows:

- (A) 1,000 grams esterified tall oil
10 grams ethyl zimate
(B) 80 grams Armac 18D dispersed in
2,910 grams of water at 65° C.

(A) and (B) jointly passed at 65° C. through a colloid mill, producing an excellent emulsion, which was diluted to 2% N. V. S. content. The ethyl zimate has the following constitution:



and is a white powder, insoluble in water but soluble in carbon disulfide, benzene, chloroform and dilute sodium hydroxide.

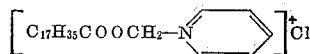
The conditioner in this case was naphthenoyl-amide—153.1, while the emulsion used was a mixture of the tall oil+zimate and acrylonitrile-butadiene in the proportions of 27 parts by weight of the tall oil (treated with the zimate) and 13 parts by weight of the acrylonitrile-butadiene. Titrations and additions followed the usual technique. Pick-up was excellent and the sheet obtained was exceedingly strong and tough.

EXAMPLE 56

A laboratory beater was furnished with unbleached Halifax kraft pulp and after brushing out the fibers for one-half hour, 5% of "Norane R"—on a solids basis—was added to the beater in the form of a 5% N. V. solids aqueous dispersion, and beating continued for one and one-half hours to produce a well hydrated stock. Thereafter, 10% of an acrylonitrile-butadiene emulsion were added to the Norane R treated stock in the beater. An instantaneous reaction took place between the Norane R treated stock and the added cationically reactive emulsion of acrylonitrile-butadiene, the liquid phase clearing in 15–20 seconds. A series of light-weight hand sheets were made 14" x 14". White water clear. No sticking tendencies at any point in processing. Sheets dried hard on hand dryer to convert Norane R to water-repellent

stage, and to cure the acrylonitrile-butadiene content. Excellent sheets resulted of tremendous degree of water resistance. This material is excellent for packaging purposes, for bag production, and a wide variety of uses in which a high degree of water resistance would be of great value. The finished sheet was washed with soap and hot water, dried in the air, and upon drying the sheet had the same waterproof qualities as originally evidenced. Repeated washings and dryings effected no noticeable change in the water-resistant qualities of the dried sheet. The sheet is definitely a washable, water-resistant paper product, of a high utility value.

The Norane-R used in this example is a tan-colored paste dispersible in water with difficulty and only at temperatures near the boiling point, say about 200° F. It is alleged to have the following formula:



and is made in accordance with United States Patents Nos. 2,261,097; 2,282,948; 2,315,135, and 2,386,631, by combining stearic acid chloride, formaldehyde and pyridine.

EXAMPLE 57

A standard 10-gram fiber suspension (1% bone dry basis) of treated fiber suspension treated with a 6% suspension of Alox 1205-X' was electrometrically titrated with a composite cationically reactive resin emulsion containing about 3 parts of Hydrocarbon Resin S-5 to 1 part of plasticized acrylonitrile-butadiene—the plasticized acrylonitrile-butadiene resin being used as a complex plasticizer for the Hydrocarbon Resin S-5. The objective of this evaluation was the manufacture of material with a zero moisture vapor transmission factor—for packaging purposes.

The acrylonitrile-butadiene resin is plasticized with a cationically reactive emulsion of dioctylphthalate on the basis of 10% dioctylphthalate solids on acrylonitrile-butadiene solids. The dioctylphthalate emulsion was added to the acrylonitrile-butadiene emulsion—before adding this complex to the emulsion of Hydrocarbon Resin S-5. For titration purposes, 450 cc. of a 2% N. V. solids cationically reactive emulsion of Hydrocarbon Resin S-5 were mixed with 165 cc. of a 2% N. V. solids cationically reactive emulsion of plasticized acrylonitrile-butadiene (100 parts acrylonitrile-butadiene solids plus 10 parts of dioctylphthalate solids).

A hand sheet was made by adding 250 cc. of the complex composite 2% N. V. solids emulsion to a 10-gram fiber suspension. Liquid phase clear; white water clear. Sheet O. K. Dried sheet to constant bone-dry weight at 215° F. and weight recorded. A blank hand sheet was made of an exact duplicate 10-gram fiber suspension—for quantitative comparisons. Sheet likewise dried to constant weight at 215° F. and weight recorded.

HAND SHEET DATA

Bone-dry weight of resin solids added-----grams--	5.00
Bone-dry weight blank hand sheet-----do-----	9.56
Bone-dry weight processed hand sheet-----do-----	15.09
Per cent solids in sheet-----per cent--	50
Per cent resin solids retention-----do-----	100

Actual sheet composition:

X-145—

- 66.66% unbleached kraft pulp
24.99% hydrocarbon resin S-5
8.35% plasticized acrylonitrilebutadiene

A series of 14" x 14" hand sheets made for evaluation. Sheets dried normally to approximately 5% moisture and calendered. Sheets excellent. Resin retentions complete. No operating troubles.

Pressed at 320° F. at 800 p. s. i. for 8 minutes, an extremely uniform resin flow resulted, the cured or flowed material being highly water-resistant, tough and flexible.

EXAMPLE 58

Using Alox L-1205-X' as the conditioning material and an emulsion containing a mixture of equal parts of paratertiarybutylphenolformaldehyde resin and an acrylonitrilebutadiene copolymer a sheet having the composition

- 72% unbleached kraft pulp
14% paratertiarybutylphenolformaldehyde resin and
14% acrylonitrilebutadiene copolymer

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was made. This was very tough and yet remained flexible when cured. It is almost completely waterproof.

EXAMPLE 59

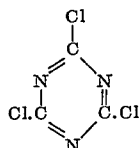
To demonstrate the utilization of the use of chlorinated rubber as a combined waterproofing agent and flame-proofer, sheets were made using fiber conditioned by means of Alox L-1205-X' and adding a cationically active emulsion of chlorinated rubber. The pick up was rapid, there being an excellent sharp endpoint and the formation of ropelike aggregations. An excellent sheet containing 40% of chlorinated rubber resulted.

EXAMPLE 60

To demonstrate the radical effect of the conditioning treatment and how the lack of it will tremendously diminish the deposition of the additaments, an untreated kraft fiber suspension had added thereto a cationically reactive emulsion of esterified tall oil. The pick up was fair for the first 10 cc. added, but then rapidly diminished. A hand sheet made retained only 9.5% of the esterified tall oil. When using an Alox L-1205-X' treated paper pulp, and operating under the same conditions otherwise, 100% retention was easily attained.

EXAMPLE 61

As a further demonstration of the wide scope of conditioning agents which may be employed, certain substances which by various reactions on cellulose may give rise to products exerting the effects of the conditioning agents may be mentioned, i. e. cyanuric chloride, which is a white crystalline solid having a melting point of 147.8° C. and a boiling point of 190° C. It is appreciably reactive with water above 10° C.—giving off an irritating toxic gas. It is considered water-insoluble, but is soluble in acetonitrile, dioxane, ether, benzene, heptane, acetic acid, ketones and carbon tetrachloride. The structural formula of cyanuric chloride is:



Accordingly, a 5% N. V. solids solution of cyanuric chloride in methyl ethyl ketone was prepared for use in evaluations and hand sheet production. The pH value of the 5% N. V. solids methyl ethyl ketone solution of cyanuric chloride was 0.

A 1,000 gram, 1% untreated fiber solids suspension of untreated beater stock was electrometrically titrated with a 5% N. V. solids methyl ethyl ketone solution of cyanuric chloride.

EVALUATION DATA

Cc. 5% N. V. Solids Methyl Ethyl Ketone Solution of Cyanuric Chloride Added to Untreated Fiber	pH Value After Addition	Comments on Liquid Phase
0	8.40	clear.
1	7.70	Do.
2	7.30	Do.
3	7.05	Do.
4	6.90	Do.
5	6.75	Do.
6	6.65	Do.
7	6.60	Do.
8	6.55	Do.
9	6.45	Do.
10	6.40	Do.
11	6.35	Do.
12	6.25	Do.
13	6.20	Do.
14	6.15	Do.
15	6.10	Do.
16	6.05	Do.
17	6.00	Do.
18	5.95	Do.
19	5.85	Do.
20	5.75	Do.
21	5.70	Do.
22	5.60	Do.
23	5.50	Do.
24	5.35	Do.
25	5.20	Do.

To an exact 1,000 gram duplicate 1% untreated fiber solids suspension (bone-dry basis) exactly 4 cc. of a 5% solids methyl ethyl ketone solution of cyanuric chloride

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were added, the mixture agitated for 15 minutes and thereafter electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene as standard procedure.

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene Added to Cyanuric Chloride Treated Fibers	pH Value after Addition	Comments on Liquid Phase
0	6.80	clear.
50 "ropes"	6.75	instant pickup—clear.
100 "ropes"	6.65	Do.
150 "ropes"	6.65	Do.
200 "ropes"	6.65	slower pickup—cleared.
250 "ropes"	6.65	slower pickup—cleared 2 min.
300 "ropes"	6.65	Do.
350 "ropes"	6.80	Do.
400 "ropes"	6.75	Do.
450 "ropes"	6.75	Do.
500 "ropes"	6.70	Do.

Hand sheet made at end of titration cycle. Liquid phase clear. White water clear. No sticking tendencies at any point in processing. Excellent, clear, well-formed sheet. Sheet dried to constant weight at 215° F.

Bone-dry weight processed hand sheet	grams	19.95
Bone-dry weight blank hand sheet	do	9.91
Per cent resin solids in sheet	per cent	100
Per cent retention resin solids	do	100

Hence, cyanuric chloride is an operable material for fiber processing in phase one of the present invention.

EXAMPLE 62

Evaluation of lauryl pyridinium chloride, or dodecyl pyridinium chloride. Lauryl pyridinium chloride is a quaternary ammonium compound; mottled tan, semi-solid, with the characteristic odor of pyridine. In aqueous dispersions the lauryl pyridinium cations are aggregated into colloidal micelles, although the dispersion looks clear to the naked eye. The molecular weight of lauryl pyridinium chloride is 292; the specific gravity is 0.99, and the surface tension of an aqueous dispersion in dynes per square centimeter, is 33. It is substantially insoluble in water. A 5% N. V. solids aqueous dispersion of lauryl pyridinium chloride was prepared for evaluation.

A 1,000 gram standard 1% untreated fiber solids suspension was electrometrically titrated with a 5% N. V. solids dispersion of lauryl pyridinium chloride, with but slight changes of pH.

4 cc. of a 5% N. V. solids aqueous dispersion of lauryl pyridinium chloride were added to a 1,000 gram 1% untreated fiber solids suspension and the mixture agitated for 15 minutes. Thereafter the mixture was electrometrically titrated with a 2% N. V. solids cationically reactive emulsion of acrylonitrilebutadiene.

EVALUATION DATA

Cc. 2% N. V. Solids Cationically Reactive Emulsion of Acrylonitrilebutadiene Added to Treated Fiber	pH Value After Addition	Comments on Liquid Phase
0	7.90	clear.
50	7.75	instant pickup—Clear.
100	7.70	Do.
150	7.60	Do.
200	7.55	Do.
250	7.45	slower pick-up—Clear 20 s.
300	7.35	Do.
350	7.30	slower pickup—Clear 30 s.
400	7.30	Do.
450	7.30	Do.
500	7.30	Do.

A hand sheet was made at the end of titration cycle, and there was no sticking or foaming tendencies, and an excellent sheet was produced, which was dried to constant weight at 215° F. Results:

Bone-dry weight of blank hand sheet	grams	9.60
Bone-dry weight of processed sheet	do	19.90
Per cent acrylonitrilebutadiene solids in sheet	per cent	100
Per cent resin solids retention	do	100

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EXAMPLE 63

The present process lends itself also to the production of composite sheets of asbestos and an elastomer or resin. To demonstrate this a long-fibered commercial asbestos fiber was cleaned by washing successively with methyl ethyl ketone, petroleum ether, ethanol and ethyl ether, dried to bone-dry weight and then leached with water to complete removal of all extraneous matter, and then dried to constant weight.

10 grams of the thus cleaned asbestos were suspended in 990 grams of water to yield 1,000 grams of a 1% suspension of asbestos. A sharp knife-like type of high speed agitator was used to defiber the asbestos and keep it in suspension. There were then added 12 cc. of a 5% N. V. S. toluene solution of Alox 1561 and the agitation continued. The asbestos fibers immediately became discolored showing the deposition thereon of the Alox 1561. The agitation was continued for 15 minutes, whereafter there were added successive 50 cc. increments of a cationically reactive emulsion of neoprene RCD-1097. There was a substantially immediate pick-up of the neoprene, the water becoming clear. Very marked rope formation occurred right from the start. A hand sheet was made without any difficulties, and dried at 215° F. The neoprene retention was 100% of that added, which was 75% of the weight of the sheet. The sheet was smooth and very tough. It was not cured but this could have readily been accomplished by heating.

EXAMPLE 64

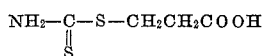
By the present invention, additaments may even be deposited upon such inert materials as glass fibers, which was demonstrated by suspending 10 grams of spun glass fibers in 980 cc. of water containing a few drops of a non-ionic wetting agent (Victawet 12 already hereinabove described). This was to insure the thorough wetting of the fibers. Thereafter 12 cc. of a 5% N. V. S. toluene solution of Alox 1561 was added to the glass fiber suspension and the mixture stirred for 15 minutes whereafter the fibers were removed from the suspension and immersed in a 2% N. V. S. cationically active emulsion of neoprene RCD-1097 for about five minutes, then removed, washed and dried to constant weight at 220° F. It was found that the glass fibers had taken up 31.5% of their weight of the neoprene. The fibers were too long to permit formation into a sheet.

EXAMPLE 65

To demonstrate the general applicability of the present invention to other than cellulosic, mineral and glass fibers, pure lamb's wool was processed. It was first treated while suspended in water with a 5% N. V. S. methanol solution of tetranaphthenoyltriethylenetetramine, using the familiar titrating procedure in a 1000 gram 1% suspension, followed by the addition of a 2% N. V. S. cationically reactive emulsion of acrylonitrilebutadiene elastomer. The wool picked up 42% of its weight of the elastomer.

EXAMPLE 66

This example produced a most unusual sheet, showing the greatest amount of "fiber-rope" formation. It was made by the usual procedure, except that the kraft pulp was washed on a 60 mesh wire to remove alkaline materials therefrom. Thereafter the stock was treated in the form of 1000 grams of a 1% aqueous suspension with 4 cc. of a 5% N. V. S. aqueous dispersion of betadithiocarbamylpropionic acid, which latter is a water-insoluble material that forms a bright lemon yellow opaque dispersion in water. Its structural formula is:



To the thus treated fiber there were added, in 50 cc. increments, a 2% N. V. S. cationically reactive emulsion of neoprene RCD-1097, a total of 250 cc. being used, as the titration was brought to an end by extremely heavy rope formation. The white water remained perfectly clear and there was no sticking on the forming wire. The sheet contained all of the added neoprene, which was 50%, showing 100% retention. The sheet was marked by its extreme toughness, even though the neoprene had not been cured.

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EXAMPLE 67

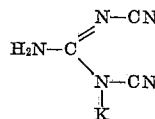
It was found that certain nitriles could be employed as conditioning materials. The nitrile employed in this example was betachloropropionitrile



which is a liquid substantially insoluble in water. An aqueous dispersion thereof was made up containing 5% of the nitrile. One thousand cc. of a 1% suspension of kraft fiber was used and 4 cc. of the nitrile solution was added thereto and the mixture agitated for 15 minutes, whereafter it was titrated with a 2% N. V. S. emulsion of acrylonitrilebutadiene elastomer. The pick-up was rapid and marked rope formation took place. The retention was 100% of the elastomer added.

EXAMPLE 68

Another somewhat analogous nitrile is potassium dicyanoguanidine



which, when used in a manner similar to that of Example 67, enabled quantitative addition of neoprene to a kraft pulp. The pick-up was also characterized by extreme rope formation, and the white water was clear. The retention was 100%.

EXAMPLE 69

Another operative nitrile is succinonitrile which is slightly water-soluble, its aqueous solutions having well developed surface active properties. Thus a 0.1% dispersion at 80° C. has a surface tension of only 35.45 dynes per sq. cm. Operating as in the previous examples, and using a 5% aqueous dispersion of succinonitrile, which has the formula



and adding 4 cc. thereof to 100 grams of a 1% kraft pulp suspension, followed by the addition of a 2% cationically reactive emulsion of acrylonitrilebutadiene solids, heavy rope formation was encountered, and the solids were quantitatively picked up to the extent of 100%. Sheet formation as usual, without any difficulties.

EXAMPLE 70

Operating in a similar manner, it was ascertained that orthotolylbiguanidehydrochloride, which is a water-dispersible white crystalline solid having a melting point of 227° C. was operative for the purposes of the present invention. Rope formation was in evidence from the start of the addition of an acrylonitrilebutadiene solids emulsion. Pick-up was rapid and 100%.

EXAMPLE 71

In this general group of materials, it was found that phenylbiguanide was also fully operative and enabled the 100% retention of acrylonitrilebutadiene solids. One of the peculiarities of this material was the increase in pH during the titration of the fiber with the phenylbiguanide. Rope formation upon the addition of the elastomer (acrylonitrilebutadiene solids) emulsion was very marked. A strong and well formed sheet resulted.

EXAMPLE 72

Also highly operative for the present purposes is guanilylurea phosphate, a crystalline solid melting at 185-188° C., which, though water-insoluble, is sufficiently dispersible to be made into a 5% dispersion, which was employed in the manner of the previous examples and served to affix an acrylonitrilebutadiene elastomer to the extent of 100% retention. Ropes formed right from the start and a very tough sheet, containing 100% of elastomer on the weight of the fibers, was formed. A peculiarity during the pick-up was that there was no applicable change in the pH of the fiber suspension.

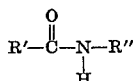
Miscellaneous operative materials

In the earlier example recited hereinabove Alox L-1205-X' was used. It has also been found that similar "Alox" materials, but differing in carbon atom chain

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lengths, are highly operative. In the next three examples, such modifications of Alox were used to affix acrylonitrile-butadiene solids, with quantitative retentions in all cases.

These Alox materials may be considered as based substantially upon the following formula



in which R' is an aliphatic chain of from 8 to 20 carbon atoms and R'' an alkyl chain of from 4 to 10 carbon atoms. The differences in the various Alox materials lie in the variations in these R' and R'' groups.

EXAMPLE 73

In this example "Alox 1560" was used. This is a water-insoluble, dark brown oily liquid, dispersible in water. In this case the 1000 gram 1% fiber suspension received successive additions of the Alox 1560 in the liquid condition as received from the manufacturer thereof, being added to the pulp in 1 cc. increments. After about 6 cc. had been added it was obvious that the end point had been reached, as small oil rings appeared on the surface of the suspension. To a duplicate 1000 grams of the suspension 2 cc. of the Alox 1560 "as is" were added, followed by incremental addition of a 2% N. V. S. emulsion of acrylonitrilebutadiene solids, 50 cc. being added at a time. Rope formation was strongly in evidence. A total of 500 cc. of the emulsion was added and then a hand sheet made. The pick-up was 100%, the sheet containing 100% of the resin on the basis of the fibers. It was one of the toughest sheets made.

EXAMPLE 74

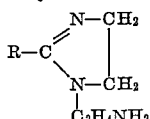
Operating in a manner substantially identical with that of Example 73, but using "Alox 1651," entirely comparable results were obtained.

EXAMPLE 75

Similar results to those obtained with the materials of Examples 73 and 74 were produced by using "Alox 1650."

EXAMPLE 76

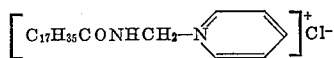
This is a further example of a complex material of the general nature of an alkylimidazoline, such as



in which the primary amino group is acetylated. This material is commercially designated as "Onyxsan"; the particular grade known as "XR" being utilized. This material is a creamy wax-like solid which in the form used, a 5% N. V. S. aqueous dispersion, yielded a thin but viscous creamy opaque dispersion. Kraft fiber beaten 1½ hours was used. The method of evaluation followed the standard procedure hereinabove frequently described. The additament was an acrylonitrilebutadiene elastomer (a "Hycar" emulsion), and the results were excellent, the amount added being 100% on the weight of the bone-dry kraft fiber, with 100% retention.

EXAMPLE 77

It is possible to employ materials which in themselves are capable of producing waterproofing effects to condition the fibers. The results are extremely interesting and highly useful products are obtained. A very striking example is the use of a material known as "Zelan AP" which has the formula



and which while soluble in the salt form appears to deposit as an insoluble material. But irrespective of theory, it was ascertained that a 5% N. V. S. aqueous dispersion of this material when applied to a kraft fiber suspension proved to be a very suitable conditioning material. Having ascertained by the usual tests that the "Zelan AP" was suitable and would effect adequate clean pick-up of acrylonitrilebutadiene copolymer solids from a cationically active emulsion thereof, 5000 grams of a 1% kraft fiber suspension were treated by adding 200 cc.

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of a 5% aqueous dispersion of Zelan AP, the suspension then being stirred for 15 minutes with a high speed mixer. Thereafter and while still mixing, 2500 cc. of a 2% cationically active emulsion of acrylonitrilebutadiene solids were added. The affixation of these solids was very rapid and the liquid had cleared in two minutes. A hand sheet was then made and dried to set the Zelan, being finally dried in an oven at 220° F. for several hours. It was found that both the Zelan AP as well as the elastomer solids had been quantitatively deposited. The product was extremely tough, waterproof, as well as water-repellent, and practically untearable. It could readily be used as a substitute for leather.

EXAMPLE 78

Using triethylenetetramine tetra-acylated with nonoic acid (3,5,5-trimethylhexoic acid) an acrylonitrile-butadiene rubber was quantitatively affixed to kraft fibers by using the technique hereinabove frequently described. The retention on an 100% addition was 100%.

EXAMPLE 79

Similar results were obtained with triethylenetetramine diacylated with 2-ethylhexoic acid, also using the acrylonitrilebutadiene rubber.

EXAMPLE 80

Similarly, the same synthetic rubber was affixed by means of triethylenetetramine tetra-acylated with 2-hydroxy-4,6,6-trimethylheptanoic acid.

EXAMPLE 81

In quite the same way triethylenetetramine tetra-acylated with a mixture of fatty acid known as "neofat 1-65" was found effective. This "neofat 1-65" is a mixture of about 90% by weight of stearic acid, about 6% of palmitic acid and about 4% of oleic acids.

EXAMPLE 82

The product known as "Sapamine WL-Ciba," when used to affix an acrylonitrile butadiene rubber to kraft fibers was found to be exceptionally efficient, particularly in so far as the properties of the finished sheet were concerned. The Sapamines are described in "Surface Active Agents" by Schwartz and Perry, 1949, pages 172-173. This was also true of another Sapamine termed "Lyofix SB-Ciba."

Further additaments

Actual tests have shown that the following additaments can be incorporated to the extent of 100% on the weight of the fibers, with 100% retention by using the technique of the present invention.

Oil-reactive phenolic resins; non-oil-reactive phenolic resins; phenolated alkyd resins; pure drying type alkyd resins; varnish types of phenolic resins; compounded neoprene synthetic rubbers; compounded "Hycar" synthetic rubbers; styrenated oils and phenolated tall oils. In all these cases, cationically active suspensions or emulsions of these materials were used, and the fiber was conditioned by the types of surface active agents hereinabove fully disclosed.

From the foregoing 82 specific examples, it will be apparent that the present invention opens up a large field of commercial and industrial applications as it enables the enhancement of the properties of fibrous materials in general, and cellulosic products, such as pulp and paper, in particular. The tremendous increase in strength of the products is but one aspect of the invention, while the increase in water-resistance, etc., is but another. While 82 examples have been given, it may be stated that over three hundred and fifty examples have been made and the products therefrom thoroughly evaluated, but these are not detailed herein in order to avoid too long a specification.

It will be quite obvious that the deposition of the various additaments, particularly strengthening materials, such as polymers, elastomers and resins, both natural and synthetic, may be applied, with but slight modifications of operative procedures, to the treatment of felted and woven fabrics, ropes, cord, knitted products such as fish nets, etc., so as greatly to increase their strength and usefulness. For the manufacture of fish line, for instance, it is a relatively simple matter to adapt the procedures to continuous pre-treatment followed by affixation of the additaments by passing the line through a cationically

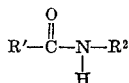
active suspension or emulsion of the additaments. A somewhat similar procedure is indicated for the treatment of continuous webs. In many cases entirely new industrial products are thus creatable, and therefore, in conclusion, some of these products are herein claimed.

In the claims which follow, the term "water-insoluble" is used in a practical rather than theoretical sense, it being appreciated that all substances are to some degree "soluble" in water. Many substances appear to dissolve in water, but actually are merely colloiddally dispersed, and only careful tests are able to discriminate between true solution and dispersion.

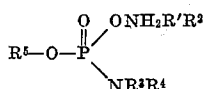
Generally speaking, therefore, the conditioning materials used to treat the fibers, such as the kraft pulp, are generally of a kind which in ordinary parlance would be considered as "insoluble." They are characterized by being able to form some kind of polarized coating on the suspended fibers, either by being directly deposited upon the fibers or by effecting a deposit of their decomposition or reaction products. In most cases they have NH_2 and NH groups in their constitution. So far as the reagents for producing the cationically active additament emulsions are concerned, these contain in almost every case a long chain amide-amine salt. It appears that this is co-deposited upon the fiber together with the additament. The fact that the white waters are clear is likewise indicative of the fact that the conditioning agent also remains on the fiber product.

I claim:

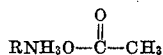
1. Process of affixing water-insoluble additaments to fibrous materials which comprises conditioning said materials by subjecting them in an aqueous environment to the action of from about 1% to about 20% of their dry weight of a cationically active substantially water-insoluble but water-dispersible highly polar surface-active agent from the group consisting of: (1) substituted amides having the general formula



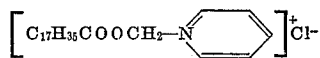
in which R' is an aliphatic group having from about 8 to about 20 carbon atoms and R^2 is an alkyl group having from about 4 to 10 carbon atoms; (2) an alkylamine salt of an alkylamide of an alkyl phosphoric acid having the structural formula:



in which R' , R^2 and R^4 represent a radical of the class consisting of hydrogen and an alkyl group, R^3 represents an alkyl group of at least 8 carbon atom chain length, and R^5 represents an alkyl group of 1 to 4 carbon atoms chain length; (3) an aliphatic amine acetate having the structure:



where R is an 18 carbon atom aliphatic chain; (4) tetranaphthenoyltriethylenetetramine; and (5) a compound having the formula

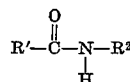


and thereafter contacting the so-conditioned materials while still in an aqueous environment with an aqueous suspension of a water-insoluble dispersed additament the particles of which carry an electropositive charge, as a result of which said particles become deposited upon and adhered to said material.

2. The process as defined in claim 1 in which the fibrous material is cellulose.

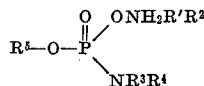
3. The process as defined in claim 2 in which the cellulose is in the form of a furnish of paper-making fibers and the process also includes as a final step the formation of paper therefrom.

4. The process as defined in claim 3 in which the surface-active agent is a substituted amide having the general formula



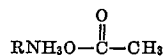
in which R' is an aliphatic group having from about 8 to about 20 carbon atoms and R^2 is an alkyl group having from about 4 to 10 carbon atoms.

5. The process as defined in claim 3 in which the surface-active agent is an alkylamine salt of an alkylamide of an alkyl phosphoric acid having the structural formula



in which R' , R^2 and R^4 represent a radical of the class consisting of hydrogen and an alkyl group, R^3 represents an alkyl group of at least 8 carbon atom chain length, and R^5 represents an alkyl group of 1 to 4 carbon atoms chain length.

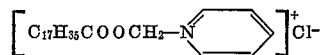
6. The process as defined in claim 3 in which the surface-active agent is an aliphatic amine acetate having the structure:



where R is an 18 carbon atom aliphatic chain.

7. The process as defined in claim 3 in which the surface-active agent is tetranaphthenoyltriethylene-tetramine.

8. The process as defined in claim 3 in which the surface-active agent is a compound having the formula



9. A fibrous product carrying permanently affixed thereto a water-insoluble additament and made by the process of claim 1.

10. A paper product made in accordance with claim 3.

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