

1

2,769,711

DEPOSITION OF TACKY IMPREGNATING AGENTS ON CELLULOSIC FIBERS

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No Drawing. Application May 14, 1952,
Serial No. 287,891

12 Claims. (Cl. 92—21)

The invention relates to the deposition of coating or impregnating materials to cellulosic fibers, to the coated or impregnated fibers obtained thereby, and to the manufacture of useful articles from the thus coated fibers. More specifically, the present invention relates to the deposition of tacky or sticky impregnating agents from aqueous dispersions or emulsions thereof on cellulosic fibers in aqueous suspension which have been treated with a cationic hydrophilic resin. More specifically still, the present invention relates to a method for preventing the formation of fibrous resin-bonded balls, clots, or aggregates during deposition of the impregnating agent as described.

The coating or impregnating of cellulosic fibers with insoluble organic, hydrophobic impregnating agents has been performed in the past by forming an aqueous stock or suspension of cellulosic fibers, adding to the stock an aqueous solution or dispersion of a cationic hydrophilic resin, and then adding the impregnating agent in the form of an aqueous emulsion or dispersion. The cationic resin causes a very uniform deposition or flocculation of the particles of the impregnating agent directly on the fibers, while preserving the drainage qualities and the felting properties of the fibers. By means of this process it has been found readily feasible to produce cellulosic felted bodies, including paper, which contain 100% and even more of the impregnating agent, based on the weight of the fibers. The felted bodies obtained are characterized by the uniformity of their content of impregnating agent, and in this process only a negligible proportion of the impregnant is lost in the white water.

In this process it is frequently desirable to allow the suspension of cellulosic fibers to stand or "age" for a period of time immediately subsequent to the addition of the cationic resin, and to defer addition of the emulsion or dispersion of the impregnating agent until adsorption of the cationic agent by the fibers has become substantially complete. This is particularly desirable in cases where large amounts of impregnating agent are deposited in comparison with the weight of the fibers. Ordinarily, during this aging the fibrous cellulosic suspension is allowed to stand for at least about 15 minutes, and longer periods have been employed to advantage.

The reason for the success of the above-described process in causing deposition of the impregnating agent while maintaining the freeness of the fibers has not been fully understood. It is believed, however, that the chief effects produced by the several steps involved are these. The cationic resin, which is always added first, is positively charged and converts the normally negatively charged fibers to a more positively charged state. The dispersion of impregnating agent, which preferably contains an anionic or a non-ionic emulsifying agent, is flocculated in the immediate presence of the more positively charged fibers causing uniform and substantially complete deposition of the impregnating agent directly on the surface of the fibers. That other mechanisms exist is demonstrated by the fact that excellent deposition of the resin occurs in numerous instances when the emulsion or dispersion of the impregnating agent is added before more than a negligible amount of the

2

cationic resin has been adsorbed by the fibers, that is, when the step of aging referred to above is omitted.

In applying the above-described process to the deposition of large amounts, that is, about 25% to 100% based on the weight of the fibers, of sticky or tacky impregnating agents, it has been found that after deposition of the dispersed particles of impregnant on the resin-treated fibers is substantially complete, and while the fibers are still in aqueous suspension, the fibers tend to form balls or clots rendering the fibers unsuitable for paper making purposes. Typically, these clots are of about the size of grains of rice and have a similar appearance.

In some instances, only a portion of the fibers in the stock clot, whereas in other instances, substantially the whole of the fibrous suspension may form itself into aggregates of this type. When clotting is extensive or complete, the value of the stock for papermaking purposes is destroyed, as it is not possible to felt a substantially clotted stock into a coherent sheet. When clot formation is slight or partial, it is sometimes possible to form a paper, but the sheets thus made are mottled and lumpy, unattractive in appearance, and of low tensile and bursting strengths.

It is a striking fact that in these clots the cellulosic fibers are almost perfectly aligned in parallel, in which position the distance between the fibers is at a minimum. It is believed that in the clotting of these fibers the impregnating agent acts as an adhesive for the fibers, bonding them together.

Despite numerous attempts, it has not been found practical to deflocculate these clots so as to regenerate a useful paper stock. Even where clotting is only partial, it has not been found practical to remove the clots so as to permit the unclotted portion of the stock to be processed in the normal manner. Up to the present, therefore, once any noticeable clotting has taken place in the stock, it has been necessary to discard the stock completely.

The emulsions of impregnating agents which so far have caused the most severe clotting are those which are formed by emulsifying a polymerizable, organic hydrophobic impregnating agent in the soft tacky stage by the use of a water-soluble soap, that is, an alkali metal, an amine, or an ammonium salt of a saturated or unsaturated fatty acid. Among these, the soaps most widely used on a commercial scale are sodium stearate, sodium oleate, and sodium palmitate, the sodium soaps of coconut fatty acids, sodium rosinat, the soaps of other rosin acids, and the sodium soap of disproportionated rosin.

Typical impregnants which are usually sufficiently tacky to cause clotting in this manner are the polymers of butadiene and styrene, styrene and ethyl acrylate, butadiene and acrylonitrile, vinyl acetate and ethyl acrylate, and esters of acrylic acid and isobutylene. These include the commercially important synthetic rubbers known as GR-S, Buna-N, Buna-S, Hycar, GR-N and Ameripol. Polymers which contain more than 50% butadiene or ethyl acrylate are particularly disadvantageous in this respect. In addition, clotting has been observed when emulsions comprising homopolymerized isobutylene in the tacky stage are employed, as well as the tacky asphalts and tars.

In general, the emulsions which are most frequently responsible for the formation of clots are those which, when dried on a glass plate at room temperature, yield films which are tacky to the touch. However, clotting frequently takes place with emulsions which contain a less tacky impregnating agent.

For example, clotting has been observed in the case of emulsions formed from impregnating agents which

are sufficiently tacky that films thereof mutually cohere when lightly pressed together. These include impregnants which are sufficiently tacky to cause "blocking," that is, the undesirable sticking together of paper impregnated therewith.

The discovery has now been made that formation of cellulosic aggregates or clots in the aforementioned process is obviated by the introduction of two simple steps in the process. In the first step, there is incorporated into the soap-containing emulsion or dispersion of the tacky impregnating agent sufficient of a stabilizing mixture to stabilize the emulsion to alum, the mixture comprising a non-ionic dispersing agent and an anionic dispersing agent selected from the group consisting of the alum-stable sulfate and the alum-stable sulfonate dispersing agents. In the second step the thus stabilized emulsions or dispersions are deflocculated and deposited on the cationic resin bearing cellulosic fibers in the presence of alum, all as will be more particularly described hereinafter.

In one embodiment of the invention the alum is added to the dispersion of impregnating agent subsequent to the addition of the stabilizing mixture, and the stabilized alum-containing emulsion is added to the cellulosic suspension previously treated with the hydrophilic cationic resin. In another embodiment the stabilizing mixture of dispersing agents is added to the dispersion of impregnating agent, the alum is added to the suspension of cellulose fibers bearing the hydrophilic cationic resin, and the stabilized emulsion is then added to the cellulosic fibrous suspension containing the alum.

In the first embodiment it is important that the stabilizing mixture of dispersing agents be added to the emulsion first, and that the alum be added only after the stabilizing agent has been uniformly distributed through the emulsion. In the second embodiment it is important that the alum be substantially uniformly distributed through the treated cellulosic suspension before the emulsion containing the stabilizing mixture is added. If these requirements are not met, unsatisfactory deposition of the resin or the formation of clots may be expected to occur.

The effect of the stabilizing mixture and of the alum on the emulsion and on the mechanism whereby the emulsified impregnating agent is deposited on the fibers, and the reason why clots do not form in the process of the present invention are not understood, and the invention should not be limited by any particular theory.

In addition to overcoming the problem of clotting, the process of the present invention has numerous distinct advantages. In the first place, the soap-containing emulsions used in the present invention are extraordinarily stable. Ordinarily, emulsions containing soap are readily flocculated by acid and electrolytes. The stabilized emulsions of the present invention, however, are acid-insensitive and fail to coagulate even when their pH is reduced to 2. Nevertheless, they display the unexpected property of flocculating in the presence of alum at that or higher pH values in the presence of the cationic resin bearing fibers, and of depositing their content of impregnating agent thereon in a uniform and most satisfactory manner. Since the pH of the cellulosic stocks upon addition of the cationic hydrophilic resin typically ranges from 3 to 5, this means that it now becomes unnecessary to adjust the pH of the stock to about neutrality prior to the addition of dispersion or emulsion as was heretofore thought necessary. Furthermore, acidic stabilizing gums may be incorporated such as alginic acid, polyacrylic acid, and carboxymethyl cellulose. Moreover, the emulsions are extremely alkali resistant. As a result, they may be added successfully when the stock has any pH up to about 12.

It is a further advantage of the present invention that the use of the stabilizing mixture of dispersing agents and alum, as described, provides a means for retarding the

rate at which the emulsion flocculates and the particles of impregnant are deposited on the fibers. The importance of this is discussed as follows.

In the ordinary case, where neither the stabilizing mixture nor alum is present, flocculation and deposition of the impregnant may take place practically instantaneously upon addition of the emulsion to the suspension of cellulosic fibers bearing the cationic, hydrophilic resin. One effect of this extremely rapid deposition is to cause a somewhat non-uniform distribution of the deposited impregnating agent throughout the stock, as the bulk of the impregnating agent is often deposited before the emulsion or dispersion can be evenly distributed throughout the fibrous suspension.

When the stabilizing mixture is employed but no alum is present either in the emulsion or in the stock, deposition of the impregnating agent on the fibers is almost always incomplete. In a few instances, substantially complete deposition of the impregnant on the fibers has taken place under these conditions, but in those instances the time required for the complete deposition has been unduly long, making the process impractical for commercial application.

When, however, alum is present either in the emulsion or in the stock, as described, deposition of the impregnating agent takes place not instantly, but expeditiously over a period of some minutes, without formation of clots and without deposition of flocs of the impregnant on the sides and bottom of the vessel. Thus the rate of deposition is retarded for a sufficient period of time to permit the dispersion or emulsion to be distributed in very uniform fashion throughout the stock while obviating the objectionable formation of clots.

More in detail, the process in its preferred embodiment is performed as follows. First a stock of papermaker's cellulosic fibers is formed at any ordinary consistency, for example, 0.5% to 5%. To this is added a predetermined amount of a cellulose-substantive, cationic, hydrophilic resin at least sufficient to cause deposition of the impregnating agent from the subsequently added emulsion. The stock is allowed to stand or age until adsorption of the resin by the fibers is substantially complete. Usually at least 15 minutes is necessary, and a much longer time may be allowed.

As cationic hydrophilic resins may be employed the cationic hydrophilic acid colloids formed by reacting melamine or melamine-urea with formaldehyde under acid conditions, as shown in U. S. Patents Wohnsiedler et al. No. 2,345,543 and Wilson et al. No. 2,563,897; the cationic hydrophilic resins prepared by reacting polyalkylenepolyamines with epichlorohydrin according to copending Daniel et al. application Serial No. 695,292, filed September 6, 1946, now U. S. Patent No. 2,601,579; the resins formed by reacting ammonium hydroxide with epichlorohydrin according to Daniel et al. copending application Serial No. 277,742, filed March 20, 1952; and the more complex resins disclosed in Daniel et al. application Serial No. 794,116, now U. S. Patent No. 2,601,598. In general, any resin possessing the same cellulose-substantive, cationic and hydrophilic characteristics of the above resins may also be employed. At least about 1/4% of the cationic resin, based on the weight of the fibers, but not more than necessary to saturate the adsorptive capacity of the cellulosic fibers therefor, is then added to the stock. In practice, this maximum is about 6% of the weight of the fibers. The suspension is then aged until adsorption of the resin is substantially complete, that is, for at least about 15 minutes and preferably 3-4 hours.

The emulsion selected for use is modified by first adding thereto a stabilizing mixture consisting of a non-ionic dispersing agent and an alum-stable anionic dispersing agent of the sulfate or sulfonate type, the ratio of two dispersing agents to each other being between about one to five parts by weight of the non-ionic agent

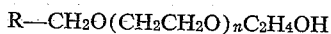
to one part of the anionic agent. The intermediate ratio of about 2.5:1 is preferred.

The amount of the stabilizing mixture which must be added to the emulsion depends on many variables, chief among which are the type and amount of soap used in the preparation of the emulsion, the tackiness of impregnating agent in the emulsion, the effectiveness of the dispersing agents of which the stabilizing mixture is composed, and the strength of the positive charges on the fibers. As a result, no exact numerical ratio has been found for correlating the amount of stabilizing mixture necessary in each instance with the above-mentioned variables. It has been found, however, that a correct amount can readily be ascertained by adding to the emulsion at least sufficient of the stabilizing mixture to stabilize the emulsion to alum. According to this method, a small amount of the stabilizing mixture is added to an aliquot of the emulsion or dispersion diluted to about 20% solids with water, followed by the addition of 5% of alum as a dilute, for example, 3% aqueous solution thereof, the percentage of alum so added being based on the weight of elastomer or impregnant in the emulsion or dispersion. If flocculation of the emulsion occurs, the test is repeated upon a fresh aliquot of the emulsion or dispersion using an increased amount of the stabilizing mixture. The end point of the test occurs when the emulsion remains stable in the presence of 5% alum, based on the weight of the elastomer or impregnant in the emulsion. If desired, there is then incorporated in the emulsion at least $\frac{1}{2}$ mol of aluminum sulfate per mol of the soap employed in emulsifying or dispersing the impregnating agent. The emulsion is then ready for use. Alternately, the alum may be added to the cellulosic stock after adsorption of the hydrophilic resin is substantially complete.

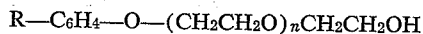
Ordinarily, commercial emulsions are supplied at a solids content of 30% to 60%. Since the process requires a uniform distribution of the emulsion in the cellulosic suspension, it is advantageous to dilute these emulsions to roughly 20%–10% solids content or lower with water. The emulsion is added to the stock of cellulosic fibers at any appropriate location as is customary and is distributed uniformly therethrough with the least amount of agitation possible.

The impregnated stock may be formed into useful products by any means known in the art. Preferably it will be sheeted as in the same manner as ordinary paper-making fibers. The water-laid sheets thus formed are then dried and cured, both steps taking place, in the case of thin sheets, when the sheet is held at about 160° F. for about 5 minutes or at about 250° F. for about 1 minute.

Any non-ionic dispersing or emulsifying agent may be used as the non-ionic component of the stabilizing mixture of the present invention. Suitable agents of this class include the reaction products of fatty alcohols or fatty acids of 8–22 carbon atoms with 6 to 50 mols of ethylene or propylene oxide to yield compounds of the formula



or $R-COO(CH_2CH_2O)_nC_2H_4OH$. In addition there may be employed the condensates formed by reacting ethylene oxide or propylene oxide with a mono or polycarboxylic acid glycol or polyglycol esters. Thus mannitol or sorbitol may be mono esterified with a fatty acid, and the product reacted with 6 to 50 mols of ethylene oxide. Moreover, the condensation products of aryl, alkaryl, cycloaliphatic and aryl-cycloaliphatic alcohols and thioalcohols with 6 to 50 mols of ethylene oxide or propylene oxide to form dispersing agents may likewise be used. Such agent may have the formula



or $R-CH_2S(CH_2CH_2O)_nCH_2CH_2OH$. In addition, the polyethyleneglycol-substituted maleic esters of the formula $HO(CH_2O)_nCH_2OCH(COOR)CH_2COOR$ may be used.

The anionic dispersing agents employed in the stabilizing mixture may be any agent selected from the well known group consisting of the alum-stable sulfonate and the alum-stable sulfate dispersing agents. Numerous members of this group are well known in the detergent art and are characterized in that $\frac{1}{2}$ % aqueous solutions thereof do not precipitate or flocculate at 20° C. in the presence of 500 p. p. m. of alum as $Al_2(SO_4)_3 \cdot 14H_2O$. Representative members of this group include the following:

- 10 Sodium alkyl naphthalene sulfonates condensed with formaldehyde
- Sodium isopropyl naphthalene sulfonate
- Sodium butyl naphthalene sulfonate
- 15 Sodium tetrahydronaphthalene sulfonate
- Sodium monobutyl phenylphenol monosulfate
- Sodium alkyl sulfobenzozoate condensed with formaldehyde
- Purified sulfolignin
- Sodium alkyl phenylene sulfonate
- 20 Sodium alkyl (ca. C_{11}) sulfonate
- Sodium octyl sulfate
- Sodium aryl alkyl polyether sulfonate
- Sodium aryl alkyl ether sulfate
- Sodium alkyl benzene mono-sulfonates
- 25 Sodium salt of N-oleyl-N-methyltaurine
- Sodium salt formaldehyde condensate of benzyl naphthalene sulfonic acid
- Sodium dodecyl phenyl poly (3) glycol ether sulfonate
- Sodium alkylanilinesulfonate

- 30 Mixtures of the two or more nonionic dispersing agents and mixtures of two or more anionic dispersing agents of the above types may also be used.

- 35 In the specification and claims the word "alum" is used to designate papermaker's alum, that is, aluminum sulfate tetradecylhydrate.

- 40 The following specific examples represent preferred embodiments of the invention, which has been disclosed above, and are not in limitation thereof. Parts are by weight unless otherwise stated.

Example 1

- 45 Bleached kraft pulp was beaten to a Green freeness of approximately 500 c. at 2.93% consistency. An aqueous dispersion of a melamine-formaldehyde colloid was prepared by dissolving 12 parts of spray-dried melamine-formaldehyde condensate (1:3 molar ratio) in 88 parts of water at 20° C. containing 0.8 mol of HCl per mol of melamine equivalent in the condensate, and aging the dispersion over night. An amount of this colloidal dispersion, containing 4% of colloid based on the weight of the fibers was stirred into the stock. The stock was then adjusted to pH 4.5 and allowed to stand for one hour.

- 50 Test emulsions were prepared from commercial GR-S type VI latex, an aqueous emulsion of the oil-in-water type having a pH of 10.0 formed by emulsifying 60 parts of a 55% butadiene-45% styrene mixture with 40 parts of water in the presence of synthetic emulsifiers and rosin soaps, and stripping off unreacted monomer. The solids content of this emulsion was about 62%. When this latex was evaporated on a glass plate, a distinctly tacky film developed. One aliquot of the latex was diluted to 10% solids with water and used as the control emulsion. The remaining aliquots were diluted to 20% solids, treated with the additives shown in the table below, and then likewise diluted with water to 10% solids.

- 65 In tests 5, 6, and 7, where alum and one or two dispersing agents were added, the dispersing agents were first thoroughly mixed with the emulsion and the alum then added as a 3% aqueous solution. The amount of alum added in each instance was equivalent to 5% of alum on the weight of copolymer in the emulsion.

- 70 The several emulsions were then added with gentle stirring to the aliquots of stock at room temperature, and the stock observed for formation of clots and rate of deposition of the copolymer on the fibers in the stock. The amounts of emulsion added in each instance con-

tained 50% of copolymer based on the weight of the fibers.

In a separate test, one part of each emulsion as described was stirred into 100 parts of water to determine the stability of the emulsions in infinitely diluted form.

shown in the table below. The stability of the emulsions in the presence of this alum was noted. The emulsions which remained stable were then further tested for stability by diluting 1 part of the emulsion with 100 parts of water. Results are shown in the table below. GR-S

Test	Emulsion Additives			Stability on Dilution	Extent of—	
	Name	Type	Percent ¹		Clotting	Latex Ppn.
1	Control			Stable	Severe	Instantaneous and complete.
2	Alum		5	Pptd.		
3	Note A	Non-ionic	5	Stable	Severe	Very slow and incomplete.
4	Note B	Anionic	3	do.	do.	Incomplete.
5	Alum		5	do.	do.	Very slow and incomplete.
6	Note A	Non-ionic	5	do.	None	Slow but complete.
7	Note B	Anionic	5	do.	do.	Rapid and complete.

¹ Based on the polymer content of the emulsion.

Note A. Condensation product of *t*-octylphenol with 10 mols of ethylene oxide.

Note B. Sodium alkyl naphthyl sulfonate condensed with formaldehyde.

Tests 1 through 4 show that the emulsions which contained only one or two of the three additives employed in tests 5 and 6 resulted in premature flocculation of the emulsion, severe fiber clotting, or incomplete deposition of the copolymer on the fibers. Test 6 shows that no fiber clotting coupled with good precipitation of the copolymer took place when the weight ratio of the components of the stabilizing mixture was at the lowest preferred ratio of 1:1.

In test 7, when the weight ratio of the components was well within the referred range, precipitation was not instantaneous, but was rapid and complete. In this example the speed of precipitation was slower than in the case of test 1, resulting in more even distribution of the impregnant throughout the cellulosic fiber suspension.

type II latex is a water emulsion having a pH of about 9.0 and a solids content of 26%–28% containing a 76.5% butadiene-23.5% styrene copolymer, prepared by the use of a sodium soap of a fatty acid as emulsifying agent. GR-S type III latex is a water emulsion having a pH of about 10.5 and a solids content of 37%–39% containing a 52% butadiene-48% styrene copolymer, prepared by the use of a rosin soap as emulsifying agent. The polyethyl acrylate emulsion was prepared by adding over 3 hours 35 parts of ethyl acrylate to 60 parts of agitated water at pH 8.5 at about 82° C. The water contained 5% sodium oleate as the emulsifying agent and 0.25% ammonium persulfate as catalyst on the weight of ethyl acrylate. The reaction was stopped 15 minutes after all the ethyl acrylate had been entered, and unreacted monomer was stripped off.

Test	Latex	Percent Stabilizing Mixture Added ¹	Percent Alum Added ¹	Stability on Addition of Alum	Stability on Dilution with 100 Parts of Water
1	GR-S type II	6.0	5	Coagulated	
2	do.	7.0	5	Flocculated; sl. coagulation	
3	do.	8.0	5	Slight flocculation	
4	do.	9.0	5	do.	Flocculated.
5	do.	10.0	5	Stable	Stable.
6	GR-S type III	6.0	5	Partly coagulated	
7	do.	7.0	5	Flocculated; coagulated	
8	do.	8.0	5	Flocculated; sl. coagulated	
9	do.	9.0	5	Sl. flocculated	Unstable.
10	do.	10.0	5	Stable	Stable.
11	GR-S type VI	3.0	5	Flocculated; coagulated	
12	do.	4.0	5	Sl. flocculated	
13	do.	5.0	5	Stable	Stable.
14	do.	6.0	5	do.	Do.
15	Polyethyl acrylate	5.0	5	do.	Unstable.
16	do.	6.0	5	do.	Do.
17	do.	7.0	5	do.	Stable.
18	GR-S type III	6.0	2	Partly coagulated	
19	do.	7.0	2	Sl. coagulated	
20	do.	8.0	2	Flocculated	Unstable.
21	do.	9.0	2	Stable	Do.
22	do.	10.0	2	do.	Stable.

¹ Based on the weight of elastomer in the emulsion.

Example 2

A series of concentrated commercial emulsions of elastomers, prepared by the use of a soap as emulsifying agent, all of which gave sticky films when evaporated on a glass plate, were diluted with water to about 20% elastomer content. To each of these was added the amount of a stabilizing mixture shown in the table below. The stabilizing mixture consisted of 70 parts of the non-ionic dispersing agent formed by reaction of *t*-octylphenol with 10 mols of ethylene oxide, and 30 parts of the anionic dispersing agent known as Accocel 740 formed by condensing sodium alkyl naphthalene sulfonate with formaldehyde. Aliquots of these emulsions were taken, and to each was added alum as a 5% aqueous solution thereof, the amount of alum added in each instance being

This table shows that the amount of stabilizing agent needed to stabilize the respective emulsions to 5% alum varied widely with the particular emulsions employed, 10% of stabilizing mixture being necessary in the case of GR-S types II and III, whereas only 5% and 6% were necessary in the case of GR-S type VI and polyethyl acrylate respectively. This table further indicates that when just sufficient of the stabilizing mixture has been added to stabilize GR-S type III latex to 2% of alum, the emulsion is thereby rendered stable to 5% of alum.

Example 3

The stabilized alum-containing emulsions of tests 5, 10, 14, 17, and 24 of Example 3 diluted to 1% elastomer

content with water were divided into two portions. One set of emulsions was acidified to pH 2 with dilute hydrochloric acid. The second set of emulsions was made alkaline to pH 12 with dilute sodium hydroxide. All emulsions remained stable under these conditions.

Example 4

Unbleached northern kraft pulp was beaten, treated with melamine-formaldehyde colloid, and aged, as described in Example 1, the proportions of colloid added, however, being as shown in the table below, and the step of adjusting the pH of the treated stock was omitted.

Emulsions of commercial elastomeric impregnating agents, having the composition set forth in Examples 1 and 2 were first diluted to 20% elastomer content, and then stabilized to alum by the addition of a stabilizing mixture formed by mixing 70 parts of the condensation product of t-octylphenol with 10 mols of ethylene oxide and 30 parts of the condensation product of sodium alkyl naphthalene sulfonate with formaldehyde. An aqueous solution containing 5% of alum as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ based on the weight of the elastomer in the emulsions, was then added. The amounts of stabilizing mixture and alum added in each instance are shown in the table below.

The resulting emulsions were then gently stirred into aliquots of the colloid-treated cellulosic stock. The pH of the stock was determined as soon as deposition of the impregnating agents had substantially ceased. Handsheets were prepared on a Nash handsheet machine. The handsheets were pressed between felts on a Noble and Wood Laboratory press and dried and cured for 8 minutes at 240° F. on a blueprint drier.

In the case of the runs with GR-S lattices, 8% of a vulcanizing agent based on the weight of elastomer was added to the stock suspension after the elastomer had been deposited on the fibers. The vulcanizing agent consisted of 12.5% ORD sulfur, 12.5% butyl zimate, 18.75% ZnO, 6.25% of the antioxidant (2,2-methylenebis-4-methyl-6-t-butylphenol), and 50% water.

Precipitation of the emulsified impregnating agent in each instance was substantially complete, and no evidence of the formation of clots was observed in the stock.

The handsheets were excellent in appearance and texture, being soft, pliable and completely homogeneous. The impregnating agents were completely deposited on the fibers in uniform condition and no balls or flocs were observed in the sheets.

Example 5

A commercial GR-S type III latex, reduced to 15% solids with water, was blended with 10% of the stabilizing mixture of Example 4, and 3% alum added as a 5% aqueous solution thereof. The quantities of stabilizing mixture and alum added were based on the weight of the latex solids. A stock of melamine resin treated fibers was prepared according to the procedure of Example 1 using unbeaten Stora 32 bleached kraft pulp, but the pH of the stock was not adjusted from the value of 3.2 which it reached after incorporation of the melamine colloid. The emulsion was then reduced to 10% solids with water and added to the stock with gentle stirring, the amount of elastomer in the emulsion being equal to 50% of the weight of the fibers. Deposition of the impregnating agent was substantially complete in 15 minutes. No clot formation occurred, and the fibers were sheeted on a handsheet machine of the type of the Noble Wood machine without adhesion to the wire or felt. The paper thus obtained was free from the effects of clots.

I claim:

1. In a method for making an impregnated cellulosic product wherein an aqueous suspension of fibrous cellulosic material is prepared, a hydrophilic cationic resin is added to said suspension, said suspension is aged until adsorption of said resin by said fibers is substantially complete, an aqueous dispersion of a water-insoluble hydrophobic organic impregnating agent in a tacky stage containing a water-soluble soap as principal dispersing agent is added to said suspension, the weight of impregnating agent in said dispersion being 25% to 100% of the weight of said fibrous material, and particles of said impregnating agent are deposited from said dispersion uniformly on said fibers by the action of said adsorbed cationic resin: the steps of adding to said dispersion of said impregnating agent sufficient of a stabilizing mixture containing about 55% to 80% by weight of a non-ionic dispersing agent and 20% to 45% by weight of an anionic dispersing agent selected from the group consisting of the alum-stable sulfonate and the alum-stable sulfate dispersing agents to render said emulsion stable in the presence of about 5% of alum, based on the weight of impregnant in said dispersion, and then depositing particles of said impregnating agent on said fibers in the presence of at least about $\frac{1}{2}$ mol of alum based on the mols of the soap in said dispersion.

2. A method according to claim 1 wherein the alum is

Test	Melamine Colloid Added, Percent ¹	Emulsion Added ²		Stabil Mixture Added, Percent ³	Percent Alum Added ³	Emul. Ppn.	Fiber Clotting	Drain. Time (Sec.)	Basis Wt. ⁴	Tensile Strength ⁵		Percent Elong.		Burst ⁶
		Type	Per-cent ¹							Dry	Wet	Dry	Wet	
1	0.0	Control					None	7	198	77.6	3.2	5.2	3.5	205
2	0.5	do					None	8	202	83.4	8.8	5.2	4.4	233
3	1.0	do					None	8.0	205	101.0	17.4	6.0	6.0	272
4	1.5	do					None	8	205	109.4	23.8	6.5	7.0	238
5	3.0	do					None	8	205	115.2	36.2	7.1	8.4	271
6	5.0	do					None	8.5	203	108.8	37.6	7.1	8.7	274
7	0.5	GRS Type II	5	10.0	5.0	Comp.	None	8	206.5	62.4	8.4	4.8	4.5	173
8	1.0	do	10	10.0	5.0	Comp.	None	8	220.5	58.4	13.6	5.7	6.8	165
9	0.5	GRS Type III	5	10.0	5.0	Comp.	None	8.5	207	72.6	9.4	6.1	5.1	189
10	1.0	do	10	10.0	5.0	Comp.	None	8	216	69.6	14.6	9.4	6.8	195
11	5.0	do	50	10.0	5.0	Comp.	None	9	289	69.0	18.4	9.4	9.6	222
12	0.5	GRS Type VI	5	5.0	5.0	Comp.	None	8	206.5	74.6	9.2	5.2	4.6	188
13	1.0	do	10	5.0	5.0	Comp.	None	8	211	67.4	12.2	6.1	6.4	203
14	1.5	do	25	5.0	5.0	Comp.	None	10	235	76.2	16.2	6.8	7.5	205
15	3.0	do	50	5.0	5.0	Comp.	None	20	293	70.0	19.8	9.0	9.5	227
16	3.0	do	50	6.0	6.0	Comp.	None	13	300	67.8	21.8	7.7	10.0	221
17	5.0	do	100	5.0	5.0	Comp.	None	28	379	69.0	24.0	9.4	11.7	227
18	0.5	Et acrylate ⁷	5	7.0	5.0	Comp.	None	10	209	80.0	10.0	5.6	5.0	225
19	1.0	do	10	7.0	5.0	Comp.	None	10	222	74.6	12.6	6.0	6.6	236
20	1.5	do	25	7.0	5.0	Comp.	None	10	250	77.0	16.0	6.8	10.7	251
21	3.0	do	50	7.0	5.0	Comp.	None	11.5	286	69.8	20.0	26.2	17.0	260
22	5.0	do	100	7.0	5.0	Comp.	None	7	384	40.0	14.2	22.9	34.9	226

¹ Based on the weight of the fibers.

² All emulsions were prepared by the use of a soap as dispersing agent.

³ Based on the weight of elastomer in the emulsion.

⁴ Lb. per ream 25" x 40"/500.

⁵ Lb. per inch.

⁶ Lb./in.² by Mullen test.

⁷ Polyethyl acrylate.

11

mixed with the stabilized dispersion of the impregnating agent, and the mixture is added to the aged suspension of fibrous cellulosic material.

3. A method according to claim 1 wherein the alum is added to the aged suspension of fibrous cellulosic material and the stabilized dispersion of impregnating agent is added to the fibrous suspension containing said alum.

4. A method according to claim 1 wherein the stabilizing mixture contains about 70% by weight of the non-ionic dispersing agent and about 30% by weight of the anionic dispersing agent.

5. A method according to claim 4 wherein the anionic dispersing agent is the condensation product of a sodium naphthylsulfonate with formaldehyde.

6. A method according to claim 1 wherein the impregnating agent is a copolymer containing more than 50% butadiene.

7. A method according to claim 1 wherein the impregnating agent is a copolymer containing more than 50% ethyl acrylate.

8. A method according to claim 1 wherein the soap is a soap of a rosin acid.

12

9. A method according to claim 1 wherein the cationic resin is a melamine-formaldehyde acid colloid.

10. A method according to claim 1 wherein the pH of the suspension of fibrous cellulosic material on addition of the stabilized dispersion of impregnating agent is 3.0 to 5.0.

11. A method according to claim 1 wherein the anionic dispersing agent is a sulfate dispersing agent.

12. A method according to claim 1 wherein the anionic dispersing agent is a sulfonate dispersing agent.

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