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METHOD OF INCREASING THE WET STRENGTH OF CELLULOSIC MATERIAL AND ARTICLE FORMED THEREBY

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This invention relates to an improved method of increasing the wet strength properties of cellulosic products and to the cellulosic products produced thereby.

It is well known to treat cellulosic materials, such as paper, prior to or following the sheet formation stage, with certain addition agents to improve the wet strength properties of the resulting products.

The term "paper" used herein is intended to include substances which are made in thin sheets or leaves from rags, straw, wood, or other fibrous, cellulosic material. Wet strength paper is paper which has been treated during its manufacture so that it retains a considerable portion of its dry strength when saturated with water. Papers which have wet strengths greater than about 15% of their dry strengths are considered to be wet strength papers.

It is known that the use of addition agents, such as amino resins, and particularly urea and melamine resins, are effective for improving or increasing the wet strength properties of fibrous cellulosic materials. However, the urea and melamine resins suffer the disadvantage that they must normally be employed under acid conditions either in the pulp beating stage or after the paper formation stage. Such acid conditions are undesirable in that they tend to cause corrosion of metal parts of the paper-making machinery, and they affect adversely the permanency of the paper products and the parts of the apparatus with which the paper comes in contact after manufacture, such as converting and printing equipment. Another group of amino resins, the guanidine resins, are not considered to be wet-strength agents for paper and therefore have not heretofore been used for this purpose. Guanidine resins have been proposed for use in paper manufacture but only in minor amounts as a modifier of other amino resins and as a coagulant for dispersions of hydrophobic polymers such as natural and synthetic latexes.

We have found that water-soluble guanidine resins are in fact effective wet strength agents when used in conjunction with a hydrophilic material which we refer to herein as a hydrocolloid. The combination of resin and hydrocolloid can be employed with important advantages in the manufacture of wet strength papers.

The combinations of the present invention can be used under neutral, acid or alkaline conditions, and they impart to the treated paper a wet strength at least equivalent to that obtained by the use of known addition agents and usually substantially greater than 15% of the dry strength of the untreated paper.

As used herein, the term "hydrocolloid" is intended to mean hydrophilic substances of the gelatin sol type as defined in Thorpe's Dictionary of Applied Chemistry, 4th Edition, volume 3, page 279, and synthetic hydrophilic substances having properties similar to those of the naturally occurring gelatin sol type of substances. These natural and synthetic substances form colloidal or near-colloidal solutions in water. Included in these "hydrocolloids" are substances which may not be hydrophilic under neutral conditions but which absorb water under alkaline conditions, for example, casein. The synthetic

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compounds are exemplified by sodium polymethylsiliconate, sold under the trade name "G.E. SC-50," and water soluble vinyl polymers. The hydrocolloids which we have found suitable for use with guanidine resins for the purpose of imparting wet strength to fibrous cellulosic material include proteins, for example, gelatin, glue, albumin, casein; carbohydrates, for example, starch, dextrin, methyl cellulose; wood products, for example, tannin and lignin; and synthetic hydrocolloids, such as sodium polymethylsiliconate, polyvinyl alcohol, polyvinyl acetate, and the polyacrylamide hydrolyte sold under the trade name "Separan 2610."

Neither the guanidine resin alone nor the hydrocolloid alone has an appreciable effect on the wet strength of pure cellulosic material compared with the result obtained with the combination of guanidine resin and hydrocolloid.

The water-soluble guanidine resins are prepared from guanidine salts and formaldehyde. A ketone, such as acetone or methyl ethyl ketone, can be used in conjunction with the formaldehyde in the preparation of the resin mixture to give the improved wet strengths characteristic of the products of the present invention.

Guanidine-formaldehyde resins suitable for use in the present invention are those in which the mol ratio of formaldehyde to guanidine is at least 2:1. This mol ratio may be substantially higher, for example, as high as 10:1, and is preferably within the range of from about 4:1 to about 5:1. With mol ratios below 2:1, the guanidine resins do not produce satisfactory results. We believe that the effectiveness of the resin-hydrocolloid combination depends on chemical reaction of the resin with the hydrocolloid and the cellulose material to be treated. The reaction may depend on the presence in the resin of free methylol or methylene groups which cause bonding of the resin to the cellulose. With ratios of formaldehyde to guanidine of less than 2:1, the proportion of free methylol or methylene groups is low, and the combination of resin and hydrocolloid is not effective as a wet strength agent.

A ketone can be used with the formaldehyde to prepare the guanidine resin. In such mixtures the mol ratio of formaldehyde to ketone should be at least 2:1, the mol ratio of formaldehyde to guanidine should be at least 1:1 and the mol ratio of formaldehyde plus ketone to guanidine should be at least 1.5:1. The ratio of formaldehyde to guanidine in such mixtures is preferably higher than 1:1, usually about 4:1 to 5:1, although ratios of 10:1 or more can be used.

Guanidine carbonate is a suitable salt for the preparation of guanidine resins which are useful for the purpose of the present invention. Other salts of guanidine such as the sulphate, the nitrate, the chloride and the acetate, can be used and derivatives such as methyl guanidine sulphate also produce good results. Other guanidine salts such as the sulphamate and the thiocyanate are less satisfactory and certain other guanidine compounds, such as diphenyl guanidine, are not suitable.

The presence of the sulphate ion is not objectionable in carrying out the process of the present invention whereas its presence is not compatible with the use of melamine resins employed in known processes for the production of wet strength paper.

The water-soluble guanidine resin can be prepared by heating, at about its boiling temperature, an aqueous solution of a guanidine salt with formaldehyde to form a syrup. Boiling is discontinued while the resin is still in the form of a syrup and before it converts to a gel. This syrup is water soluble and can be used as such or it can be diluted for convenience in handling or metering; or it can be evaporated, for example, under vacuum,

to form a water-soluble solid for convenience in shipping or storage. The resin can be added as an aqueous solution to the cellulose stock to be treated.

The manner in which the guanidine salt-formaldehyde heating step is conducted is important. It should be terminated before the resulting syrup commences to form a gel. Prolonged heating results in the formation of a gel and finally a solid. The formation of a gel or solid in the heating step is an indication that resin condensation has progressed too far; the resultant condensation product is not water soluble and is unsuitable as an additive for cellulose treatment to increase the wet strength of the desired product.

The water-soluble guanidine resins can be used without the addition of a hydrocolloid for treating pulps such as unbleached kraft and ground wood pulp, probably due to the presence in such pulp of hydrocolloid material such as lignin or tannin. However, we have found that substantially improved results are obtained even with these pulps by the combination of a water-soluble guanidine resin and additional hydrocolloid.

Fillers, sizes and other addition agents usually are employed in the manufacture of fibrous cellulosic materials to improve desired properties in the resulting product. Fillers such as calcium carbonate and zinc oxide cannot readily be used under the acid conditions normally required by urea and melamine resins in the manufacture of wet strength papers, although some fillers, such as titanium dioxide and clay, are compatible with such acid conditions. An important advantage of the use of the guanidine resin-hydrocolloid combination of this invention is that the combination is not restricted to use under any specific condition of hydrogen ion concentration but can be employed over a wide range of hydrogen ion concentrations, for example, from about pH 3 to pH 11, and is compatible with the fillers, sizes and other addition agents conventionally employed in the manufacture of fibrous, cellulosic products. In this regard, we have found that in some cases the use of the guanidine resin-hydrocolloid combination of the present invention, for example, guanidine resin and Separan, increases the percentage retention of the fillers in the final cellulose products.

The guanidine resin-hydrocolloid combination can be incorporated into the cellulosic stock at any convenient stage of manufacture of the desired product, that is, at the beater, or the stock chest or the head tank. It can be used as a stream, as a tub size, or as a spray. For economy of equipment and convenience of operation, it is preferred to make the addition to the pulp at the beating stage.

The conditions under which the method of the present invention can be operated can be varied relatively widely. The pH range of the aqueous suspension of fibrous, cellulosic pulp in which the water-soluble guanidine resin is employed can be from about pH 3 to about pH 11, but is usually from about pH 6 to pH 8, and is preferably from about pH 7 to about pH 8 in order to obtain the advantages for both the product and equipment of neutral or slightly alkaline conditions. There is no need in our process for the alum treatment commonly used with other wet strength additives, such as melamine and urea resins.

The amount of water-soluble guanidine resin employed can vary from about 0.1% to 10% by weight based on the dry weight of the cellulosic material to be treated, and is usually larger than the amount of hydrocolloid required. The amount of hydrocolloid present in the pulp suspension can be from about 0.02% to about 10% or more of the dry weight of the cellulosic material, depending on the particular hydrocolloid used, and whether substances having hydrocolloidal properties are present in the pulp. For example, in the manufacture of paper and hardboard from unbleached kraft pulp, it is not so essential to add a hydrocolloid with the guanidine resin,

probably due to the presence in the pulp of a hydrocolloid substance which produces similar results, for example, lignin or tannin. However, even in this case, additional hydrocolloid is very effective. Generally, in the treatment of cellulosic materials, very satisfactory results are obtained with from about 1% to about 10%, by weight, of the water-soluble guanidine resin and from about 1% to about 5%, by weight, of the hydrocolloid. The ratio of resin to hydrocolloid is usually about 2:1. This particular ratio can be varied widely, of course, depending on the hydrocolloid employed.

The resin should be "aged" to obtain the highest wet strengths in the resulting fibrous cellulose products. The aging process merely involves storing the resin as solution, i.e. syrup, or as a solid under normal atmospheric temperature and pressure conditions for a period of from about one to seven days during which condensation of the resin proceeds to the stage at which the resin produces the best results in improving the wet strength of the fibrous cellulosic material. It is merely necessary, in order to determine the aging period for a specific resin, to conduct small scale tests with samples of cellulose stock and observe the results obtained. After aging, the resin retains its activity for several months.

The following examples illustrate methods of preparing water-soluble guanidine resins suitable for use in this invention:

EXAMPLE 1

5.8 grams of acetone, 33.8 grams of formaldehyde (40% solution) and 0.5 ml. of 20% sodium hydroxide solution were mixed and heated at about 40° C. for a period of time sufficient for the reaction between the constituents to take place. The mixture was then boiled for about 10 minutes under a reflux condenser. 13.5 grams of guanidine carbonate in 50 ml. of water were added to the mixture and the resulting mixture was boiled for 15 minutes and then diluted with water to 200 ml. The resulting resin syrup was aged for 7 days.

EXAMPLE 2

45 grams of formaldehyde (40% solution), 18 grams of guanidine carbonate and 25 ml. of water were mixed and boiled for 1 hour under a reflux condenser and the resulting resin syrup was diluted with water to 200 ml. The aging period of this resin syrup was 7 days.

EXAMPLE 3

5.8 grams of acetone, 33.5 grams of formaldehyde (40% solution) and 1 ml. of 20% sodium hydroxide solution were boiled under a reflux condenser for 10 minutes. 16.2 grams of guanidine sulphate and 5.6 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) dissolved in 50 ml. of water were added to the mixture and the resulting mixture was boiled for ten minutes and then diluted with water to 200 ml.

EXAMPLE 4

The same procedure was followed as in Example 3 but using only 3.8 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$).

EXAMPLE 5

The same procedure was followed as in Example 3 but the guanidine resin syrup, after boiling, was cooled and evaporated to dryness under a vacuum.

EXAMPLE 6

5.8 grams of acetone, 45.0 grams of formaldehyde (40% solution), and 1 ml. of 20% sodium hydroxide solution were mixed and boiled for 10 minutes. 21.6 grams of guanidine sulphate and 12.4 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) dissolved in 50 ml. of water were added to the mixture and the resulting mixture was boiled for 10 minutes and then diluted with water to 200 ml.

EXAMPLE 7

The same procedure was followed as in Example 3, but using 7.5 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$).

EXAMPLE 8

The same procedure was followed as in Example 3, but using 9.3 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$).

The sodium compounds used in Examples 1, 3, 4, 5, 6, 7 and 8 above were added to adjust the pH value of the resin mixture to ensure a value of not less than pH 7. We have found that the pH of the guanidine resin mixture should be 7 or higher, preferably 10 to 10.5, for satisfactory results. It may be that with pH values less than 7, condensation of the resin proceeds too far. Although the pH of the guanidine resin should not be less than 7, the pH of the pulp solution to which the resin is added may vary from about pH 3 to about pH 11, as noted previously.

In the use of the guanidine resin addition agents, the resin solution is added to a water suspension of cellulose pulp in amount corresponding to about 5%, for example, based on the dry weight of the pulp. A hydrocolloid, such as gelatin, in amount corresponding to 2.5%, for example, of the dry weight of the pulp, is added to the pulp suspension as a solution in water at the same time as the resin, and the pulp suspension is then thoroughly mixed. The usual sheet-forming and drying steps follow. With relatively crude pulps the hydrocolloid is less essential, as noted previously, but is beneficial.

For best results, the resultant fibrous cellulosic product should be "cured" after drying, or the curing may be incorporated in the drying stage. Curing is effected by heating the product for a time which varies with the temperature. A time period of one hour at about 90° C. is satisfactory. Longer times, up to several days, may be required at lower temperatures, such as 70° C., and shorter times at higher temperatures.

The hydrocolloid can be added to the pulp suspension before, with or after the resin, or the resin and hydrocolloid solutions can be mixed and the mixture added to the suspension. It may be convenient to use such mixtures, which can be stored for periods up to 24 hours without impairing their effectiveness, but usually the resin and hydrocolloid are added to the pulp suspension separately at the same stage of operation, preferably at the beater.

The following table illustrates the results obtained in wet strength tests using different combinations of water-soluble guanidine resins and hydrocolloids with different cellulosic pulps. The percentage figures for resin and hydrocolloid are based on the dry weight of the pulp. The resin solutions numbers in the table correspond to the preceding examples, solution No. 1 being prepared according to Example 1, solution No. 2, according to Example 2, etc. The letter "K" applied to the furnish stands for unbleached kraft pulp, "R" for highly refined pulp, such as almost pure cellulose pulp, and "S" for bleached sulphite pulp.

The testing procedure consisted of beating a furnish containing about 1.5 grams of pulp, 400 ml. of water and the stated amounts of resin and hydrocolloid for two minutes, then draining the water through a screen. The resulting sheet was sucked free of water, pressed with a load of 250 pounds per square inch for twenty seconds and dried and cured at 100° C. for two hours. The dried and cured sheet was soaked in water for five minutes. Excess water was removed by placing the sheet on blotting paper for 10 minutes. Wet strength measurements were then made using a Mullen bursting tester. These measurements gave the figures in the "Wet strength" column of the table. For dried sheets prepared in the same manner but not treated with resin or hydrocolloid, and not subjected to the soaking step, the Mullen measurements were 13, 25 and 20 for paper

prepared from unbleached kraft pulp, highly refined pulp and bleached sulphite pulp, respectively.

Table I

No.	Wt. per cent	Guanidine Resin		Hydrocolloid		Furnish		Wet Strength
		Material	Wt. per cent	Type	pH			
10				R			0	
				S			0	
				K			0	
1	10	Gelatin	10	R	7.0		40	
		do.	2.5	K	7.8		0	
15	5	do.	2.5	K	7.8		36	
1 ^b	5	do.	2.5	K	8.0		51	
1 ^c	5	do.		K	8.0		15	
4	5	Gelatin	2.5	S	7.2		45	
4	2.5	do.	1.0	S	7.0		35	
4	5.0	do.	2.5	S	7.2		49	
5	5.0	do.	5.0	R	6.8		18.5	
2	5.0	do.	10	R	7.5		0	
20	5	Potato Starch	2.5	R	7.6		22	
3	5	do.	2.5	R	8.0		23	
2	10	do.		R	7.0		0	
3	5	Hydroxyethyl Starch	2.5	R	8.0		15.5	
		do.	2.5	R	8.0		0	
4	5	Separan	2.5	S	7.6		75	
3	5	do.	0.02	R	8.0		9	
3	5	do.	0.5	R	6.8		23	
25	5	do.	2.5	R	7.2		30	
3	5	do.	2.5	R	7.6		0	
4	5	Sodium polymethylsiliconate	2.5	S	7.6		40	
		do.	2.5	S	7.4		1	
6	5	Gelatin	2.5	R	4.0		3	
6	5	do.	2.5	R	6.0		11.5	
6	5	do.	2.5	R	7.6		14	
6	5	do.	2.5	R	9.0		3.5	
30	5	do.	2.5	K	5.0		5	
6	5	do.	2.5	K	6.0		26	
6	5	do.	2.5	K	10.0		13	
6	5	do.	2.5	S	4.0		6.5	
6	5	do.	2.5	S	6.0		21	
6	5	do.	2.5	S	10.5		5	
6	5	do.	2.5	S	7.2		28	
35	5	Lignin	2.5	R	8.5		4.5	
4	5	Alpha protein	2.5	R	8.0		9	
7	5	Casein	2.5	R	8.0		9	
8	5	Karaya gum	2.5	R	7.0		11	

^a 3 ml. 5% $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ solution added when beating the pulp.

^b 3.5 ml. 5% $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ solution added when beating the pulp; furnish beaten for 3.5 min.

^c 3.5 ml. 5% $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ solution added when beating the pulp.

A list of the hydrocolloids that we have found to be suitable for the purpose of the present invention includes the following:

45 Carbohydrates: starch, dextrin, karaya gum, guar gum, locust bean gum, gum arabic, gum tragacanth, hydroxyethyl starch, hydroxyethyl cellulose, methyl cellulose, sodium carboxymethyl cellulose, sodium alginate, Chinese vegetable gelatin;

50 Proteins: gelatin, glue, zein, egg albumin, blood albumin, soy bean flour, soy bean protein (alpha protein), casein;

Wood hydrocolloids: lignin, Goulac (calcium lignin sulphonate), tannin;

55 Synthetic hydrocolloids: polyvinyl alcohol, polyacrylamide, partially degraded polyacrylamide (by Hofmann reaction), polyacrylamide hydrolyte (Separan 2610), polyvinyl pyrrolidone, polyvinyl methyl ether/maleic anhydride copolymer, styrene/maleic anhydride copolymer

60 (Stymer S), sodium polymethylsiliconate.

The present invention possesses a number of important advantages. The water-soluble guanidine resin can be prepared easily and inexpensively under moderate operating conditions. The use of a water-soluble guanidine resin in conjunction with a hydrocolloid in accordance with the present invention results in a substantial improvement in both the wet strength and dry strength of treated fibrous cellulosic material. The combination of resin and hydrocolloid possesses the added important advantage that it can be used with fibrous cellulosic pulp mixtures over a wide range of hydrogen ion concentrations of from about pH 3 to about pH 11 thus permitting its use with acid, neutral or alkaline pulp mixtures.

It will be understood, of course, that modifications can be made in the embodiments of the invention described

herein without departing from the scope of the invention as defined by the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States of America is:

1. In a process for increasing the wet strength properties of fibrous cellulosic material, the improvement which comprises the step of treating said fibrous cellulosic material with a combination composed of water soluble guanidine-formaldehyde resin and a hydrocolloid, the formaldehyde being present in said resin in the ratio of at least about 2 mols per mol of guanidine, said resin being provided in amount of at least about 0.1% by weight based on the dry weight of the fibrous cellulosic material, and said hydrocolloid being provided in amount of at least about 0.02% by weight based on the dry weight of the fibrous cellulosic material.
2. The process according to claim 1 in which the hydrocolloid is a member selected from the group consisting of proteins, carbohydrates, wood hydrocolloids and synthetic hydrocolloids.
3. The process according to claim 1 in which the hydrocolloid is a member selected from the group consisting of gelatin, starch, lignin, polyacrylamide hydrolyte and sodium polymethylsiliconate.
4. The process according to claim 1 in which the guanidine-formaldehyde resin is provided in amount within the range of from about 0.1% to about 10% by weight based on the dry weight of the fibrous cellulosic material.
5. In a process for producing paper which comprises forming an aqueous pulp of fibrous cellulosic material, removing water from said pulp and forming said pulp into a sheet, the improvement which comprises providing in said pulp a combination composed of water soluble guanidine-formaldehyde resin and a hydrocolloid, the formaldehyde being present in said resin in the ratio of at least about 2 mols per mol of guanidine, said resin being provided in amount of at least about 0.1% by weight based on the dry weight of the fibrous cellulosic material, and said hydrocolloid being provided in amount of at least about 0.02% by weight based on the dry weight of the fibrous cellulosic material.

6. In a process for producing paper which comprises forming an aqueous pulp of fibrous cellulosic material, removing water from said pulp and forming said pulp into a sheet, the improvement which comprises providing in said pulp a combination composed of water soluble guanidine-formaldehyde-acetone resin and a hydrocolloid, the formaldehyde being present in said resin in the ratio of at least about 2 mols per mol of acetone, the formaldehyde plus acetone being present in the ratio of at least about 1.5 mols per mol of guanidine, said resin being provided in amount of at least about 0.1% by weight based on the dry weight of the fibrous cellulosic material, and said hydrocolloid being provided in amount of at least about 0.02% by weight based on the dry weight of the fibrous cellulosic material.
7. A fibrous cellulosic material treated with a combination of guanidine-formaldehyde resin and a hydrocolloid, the formaldehyde being present in said resin in the ratio of at least about 2 mols of formaldehyde per mol of guanidine, said resin being present in amount of at least about 0.1% by weight based on the dry weight of the fibrous cellulosic material, and said hydrocolloid being present in amount of at least about 0.02% by weight based on the dry weight of the fibrous cellulosic material.

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