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Coscia et al.

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[54] PULPING OF WET STRENGTH BROKE CONTAINING POLYVINYLAMIDE-GLYOXAL RESIN

[72] Inventors: **Anthony Thomas Coscia**, South Norwalk; **Laurence Lyman Williams**, Stamford, both of Conn.

[73] Assignee: **American Cyanamid Company**, Stamford, Conn.

[*] Notice: The portion of the term of this patent subsequent to Jan. 19, 1988, has been disclaimed.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 745,486, July 17, 1968, Pat. No. 3,556,932, which is a continuation-in-part of Ser. No. 471,463, July 12, 1965, abandoned.

[52] **U.S. Cl.** **162/4**, 162/166

[51] **Int. Cl.** **D21h 3/52**

[58] **Field of Search** 162/4, 5, 6, 166, 168

[56] **References Cited**

UNITED STATES PATENTS

3,556,932	1/1971	Coscia et al.	162/166
2,394,273	2/1946	Thomas	162/4
2,872,313	2/1959	House et al.	162/6
3,245,868	4/1966	Espenmiller	162/4

Primary Examiner—S. Leon Bashore
Assistant Examiner—Frederick Frei
Attorney—Evans Kahn

[57] **ABSTRACT**

Wet strength paper broke composed of fibers bonded together by a wet strength polyvinylamide-glyoxal resin in thermoset state is pulped by contacting the broke with an aqueous medium substantially free from oxidizing agent having a pH between 5 and 10 and a temperature above 100° F. and subjecting the broke to mechanical pulping.

7 Claims, No Drawings

PULPING OF WET STRENGTH BROKE CONTAINING POLYVINYLAMIDE-GLYOXAL RESIN

This is a continuation-in-part of our copending application, Ser. No. 745,486, filed July 17, 1968 now U.S. Pat. No. 3,556,932, which is a continuation-in-part of our application Ser. No. 471,463, filed July 12, 1965 which was copending therewith and which is now abandoned.

The present invention relates to the pulping of wet strength paper broke composed of cellulose fibers carrying a polyvinylamide-glyoxal resin as agent imparting wet strength, so as to form a fibrous suspension which possesses intrinsic wet strengthening properties and which can be sheeted either alone or in admixture with fresh pulp with or without additional wet strength resin, to produce wet strength paper. The invention includes papermaker's pulp having a content of said resin and the manufacture of wet strength paper by use thereof. In this specification the reference to fibers which possess "intrinsic wet strengthening properties" means that the fibers act in the same manner as wet strengthening resins when they are added to an aqueous suspension of resin-free cellulose papermaking fibers and the resulting furnish is processed into paper.

The commercial necessity for the pulping of wet strength broke and methods therefor is disclosed in Thomas U. S. Pat. No. 2,394,273, Goehler et al. U. S. Pat. No. 2,423,097, House et al. U. S. Pat. No. 2,872,313, Maxwell U. S. Pat. No. 3,407,113 and Espenmiller U. S. Pat. No. 3,245,868. The processes of these patents involve the use of acids, high pressure steam, and specially designed apparatus.

The pulp from these processes possesses substantially no inherent wet strengthening properties, and therefore, paper made from the pulp (in the absence of added materials) possesses substantially no wet strength. Evidently the pulping processes of these patents causes hydrolysis of the wet strength resin contents of the pulps and consequently destroys their wet strengthening properties.

The discovery has now been made that wet-strength paper broke composed of fibers bonded together by a content of a normally water-soluble thermosetting ionic wet-strength polyvinylamide glyoxal resin is pulped more rapidly yet with greatly minimized destruction of said resin by subjecting the pulp, with exclusion of oxidizing salts and oxidizing acids, to an aqueous medium having a specified elevated temperature and a specified low pH. The process is preferably performed by the use of aqueous medium having a temperature in excess of 100° F. and a pH between 5 and 10, with simultaneous or subsequent mechanical pulping of the thus-treated broke.

In preferred embodiments, the pulping process of the present invention possesses the following advantages:

1. The process is simple. No special reagents or mechanical equipment is required.

2. The process is harmless to the color of paper containing oxygen-sensitive dyes and pigments such as ultramarine. However, it tolerates bleaching agents when present in normal amounts.

3. The process is comparatively harmless to the fibers. It does not hydrolyze or otherwise weaken the cellulose to a significant extent.

4. The process is astonishingly rapid. In preferred instances, complete fiber liberation is achieved in less than one minute. As a result, the pulping tanks are more efficiently used and in any instance, these tanks can be of substantially smaller capacity than heretofore thought practical.

More in detail, according to one embodiment of the present invention, paper broke composed of cellulose fibers bonded together by an adsorbed content of a normally water-soluble thermosetting ionic polyvinylamide-glyoxal polymer in at least partially reacted, partially thermoset state (i.e., the state wherein at least some of the polymeric macromolecules have reacted with the cellulose and at least some thereof have cross-linked in normal thermosetting manner) is pulped according to the present invention by contacting the broke (hereinafter termed for convenience "polyvinylamide-glyoxal broke") with aqueous medium within the temperature and pH range mentioned until the fiber-polymer bonds have loosened to the point where the fibers can be separated by mechanical pulping. The broke is then subjected to mechanical pulping to ensure total separation of the fibers. According to another embodiment, the pulp is subjected to mechanical pulping action while the aqueous medium is loosening the fiber-polymer bonds.

The temperature of the aqueous medium in which the pulping process is performed is of importance. The temperature may extend from room temperature to the boil with, however, different results. A low temperature (e.g., about 100° F.) is used when a comparatively slow rate of fiber liberation is acceptable and when it is desired that the polymer on the fibers retain as much of its original dry and wet strengthening properties as practical, so when the fibers are remade into paper the polymer on the fibers will continue to exert a wet and dry strengthening effect. A high temperature (e.g., above about 140° F.) causes rapid fiber liberation, particularly when the pH of the aqueous medium is high.

The pH of the aqueous medium is likewise of importance. A low pH (e.g., about 5) prevents degradation of the wet and dry strength properties of the fiber but results in a comparatively slow fiber liberation rate. A higher pH results in an acceleration of the fiber liberation rate, particularly when the aqueous medium is at elevated temperature, but decreases the wet and dry strength properties of the fibers. A pH of 10 is regarded as the maximum which produces commercially acceptable results.

The time during which the broke is in contact with the aqueous medium is sufficiently long so that the fiber-resin bonds are loosened to the point where the fibers can be rapidly and completely liberated by available mechanical pulping equipment. This is a function of the particular polymer present on the fibers, the age of the broke, the particular mechanical equipment available, and the pH and temperatures used. The appropriate time in each instance can be determined by testing the broke every few minutes. However, there is no advantage in delaying mechanical pulping until the action of the aqueous medium is complete, and in practice the mechanical action is started shortly after the broke has been charged into the pulping medium, so that testing of the pulp becomes unnecessary.

The relationship of the foregoing variables is shown qualitatively in the following table:

	Pulping conditions			Rate of fiber liberation	Fiber	
No.	Temp.	pH	Time		W/S properties	Dry strength
1	Low	Low	Longest	Slow	Best	Best.
2	Low	High	Short	Fast	Low	Good.
3	High	Low	Short	Fast	Very good	Good.
4	High	High	Shortest	Fastest	Low	Least.

It will be seen that best results in terms of the wet and dry strengthening properties of the fibers are achieved by the use of low temperature and low pH, that rapid fiber liberation occurs with preservation of the strengthening properties of the fibers when the temperature of the aqueous medium is elevated, and that fastest fiber liberation occurs when both the temperature and the pH of the aqueous medium are high.

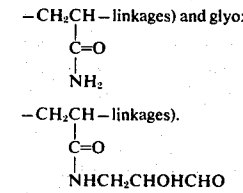
The aqueous medium may consist of plain water adjusted to the desired pH and temperature, but may contain one or more biocides to prevent formation of slimes, wetting agents to accelerate wetting-out of the broke, and a buffer to maintain the pH at a desired level. The aqueous medium should contain no oxidizing agent as it is without significant effect on the pulping rate. Sufficient water is present so that a mobile slurry is achieved, and this generally requires a consistency of less than 10 – 15 percent.

The process of the present invention includes steps which are conventionally employed in the pulping operation, for example, slicing large rolls or blocks of broke into portions which are more easily wetted; shredding or otherwise comminuting the broke prior to treatment; adding a wetting agent and/or a dispersant to the aqueous pulping medium to accelerate wetting of the broke and dispersion of liberated fibers; adding a dye or pigment to produce a pulp of apparently uniform color; and adding a biocide to prevent formation of slimes. These steps do not alter the essential character of the process.

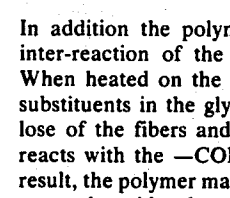
It is a surprising feature of the invention that it permits paper pulp (such as is sold to papermakers as raw material for the manufacture of paper) to be used as a wet strengthening agent. Such pulp is a water-laid web of cellulose fibers, usually bleached and often beaten to papermaking freeness, and is usually sold in the form of compressed bales or rolls. We have found that such pulp may have a uniformly absorbed content as latent wet strengthening agent of up to about 3 – 5 percent based on the dry weight of the fibers of an ionic polyacrylamide-glyoxal wet strength resin, that such pulp having a water content of 20–30 percent by weight can be stored for long periods of time without significant detriment to the latent wet strengthening properties of the resin therein, that said pulp can be readily dispersed into its component fibers without detriment to the polymer therein by slushing in water having a pH of 5–7 and a temperature of 20° – 100° F., and that paper of satisfactory wet strength is obtained when a quantity of the resulting fibrous suspension and a quantity of a virgin fibrous suspension are mixed and the mixture is processed into paper as herein described. The absorbed polymer on the fibers provides about 80 percent of the wet strength which it would provide if added to the fibrous suspension in customary manner (e.g., at the headbox).

The discovery described above for the first time makes it possible for paper manufacturers to manufacture wet strength paper without need to receive, handle, store and meter wet strength resin solution.

The polymer present in the broke which is pulped according to the present invention in normal state (i.e., as manufactured and before use) is at least half (molar basis) composed of vinylamide linkages (e.g.,



–CH_2CH– linkages) and glyoxylated vinylamide linkages (e.g.,



–CH_2CH– linkages).

In addition the polymer may contain link-ages formed by inter-reaction of the vinylamide and glyoxylated linkages. When heated on the fibers, a portion of the —CHOHCHO substituents in the glyoxylated linkages react with the cellulose of the fibers and a portion of the glyoxylated linkages reacts with the $—CONH_2$ substituents of the polymer. As a result, the polymer macromolecules become cross-linked, and are anchored by chemical reaction with the fibers. Before and after application to the fibers, the polymer contains one or more cationic linkages (e.g., those derived from diallyldimethyl ammonium chloride, and dimethylaminoethyl acrylate quaternized with methyl chloride). A variety of suitable copolymers is disclosed in our said copending application, which is hereby incorporated by reference in the present application.

The process is more fully described in the examples which follow. These examples are best embodiments of the invention and are not to be construed in limitation thereof.

EXAMPLE 1

The following illustrates the pulping of wet strength broke according to the present invention.

The broke is paper having a basis weight of 50 lb. per 25 × 40 inches/500 ream composed of cellulose fibers bonded together by 1 percent based on the dry weight of the fibers of a 97.8 : 2.2 molar ratio acrylamide :diallyldimethyl ammonium chloride polymer which had been reacted with glyoxal so that the ratio of glyoxal substituents on the backbone to the amide substituents is about 0.12 : 1. The paper has a wet strength of 8.0 lb./inch after 15 minutes of immersion in water having a temperature of 20° C. and a pH of 7, and is prepared according to Example 11 of said copending application.

A. A 50 g. portion of the broke cut into ½-inch squares is slurried in 1,000 cc. of water at 25° C. and pH 9 for 30 minutes. At the end of that time the fiber-polymer bonds in the paper have extensively loosened. The slurry is then mechanically pulped by slushing for a few minutes in a laboratory Valley beater, after which liberation of the fibers is complete.

Good quality wet strength paper is obtained when the resulting pulp is diluted to 0.6 percent consistency, sheeted on a Nash handsheet machine at 50 lb. basis weight and dried on a laboratory drum drier having a drum temperature of 240° F.

B. The foregoing is repeated except that the temperature of the water is 160° F. and the pH of the aqueous medium is 12. The broke pulps almost instantly.

C. The resulting broke is made into paper without addition of resin. The resulting paper possesses substantially no wet strength.

EXAMPLE 2

The procedure of Example 1 is repeated except that the pH of the slurry is decreased to 7 and the temperature of the aqueous medium is 150° F. Fiber liberation is substantially complete in 20 minutes

The resulting broke is made into paper without addition of resin. The resulting paper possesses very satisfactory wet strength.

EXAMPLE 3

The following illustrates the comparative effects of temperature and pH on the pulping of wet strength broke according to the present invention. In this example the action of the aqueous medium and mechanized agitation proceed simultaneously.

The wet strength broke are cut-up laboratory handsheets of about 70 lb. basis weight per 25 × 40 inch/500 ream containing 1 percent by weight of a water-soluble cationic thermosetting glyoxylated polyvinylamide in thermoset state (the reaction product of a 100 : 6.5 molar ratio acrylamide : diallyldimethyl ammonium chloride copolymer with about one-fourth mol of glyoxal per mol of acrylamide linkages in said copolymer). The broke has a wet strength of 7 – 8 lb. per inch when tested as described in Example 1.

In each test, 2.5 g. of the cut-up handsheets (composed of squares about one-half inch per side) are placed in a Waring blender containing water having the pH and temperature shown in the table below, and the blender is run at slow speed for three minutes. The blender is then stopped, the slurry is diluted to 1 liter with water, and the extent to which the broke has been pulped is determined by examining the aqueous medium for unpulped paper and fiber bundles. A rating of 0 – 1 indicates substantially complete pulping (substantially no fiber bundles) and a rating of 10 indicates that no pulping whatever occurred, substantially all the squares being in their original form. Intermediate numbers indicate proportional intermediate results. Values of 4 or lower are commercially acceptable.

The acid pH adjustments are made by addition of alum or sulfuric acid and the alkaline pH adjustments are made by addition of sodium carbonate or sodium hydroxide.

Run No.	Pulping medium pH	Pulping medium °F.	Fiber liberation after 3 minutes Rating	3 minutes Description	Fiber liberation after 10 minutes Rating	10 minutes Description
1	4.0	75	7	Slight	3	Almost complete.
2	7.0	75	6	Moderate	2	Few bundles.
3	10.0	75	3	Almost complete	1	Complete.
4	4.0	175	2	Nearly complete		
5	7.0	175	1	Complete		
6	10.0	175	1	do		

EXAMPLE 4

The procedure of Example 3 is repeated except that (1) the broke used is prepared from 50:50 bleached hardwood: bleached softwood handsheets having a basis weight of 70 lb. per ream made by beater addition of 0.5 percent of the wet strength polymer, and (2) the progress of the pulping is determined by removing samples at intervals as shown in the table below, diluting the samples with water and determining the time at which complete fiber liberation is achieved.

Results are as follows:

Run No.	Temp. pulping medium °F.	Time to achieve complete fiber liberation at: pH 4.0	pH 7.0	pH 8.5	pH 10.0	pH 11.5
1	77	88′	45′	31′	12′	5′
2	145–150	18′	8′	5′	40″	25″

Comparison between the results of Examples 3 and 4 shows that while it is possible to achieve complete fiber liberation with low temperature water (i.e., below 100° F.) and at pH values below 9, much more rapid pulping is obtained both by the use of temperatures above 100° F. and pH values above 9, and that most rapid fiber liberation is achieved by the use of high temperature and high pH in combination.

EXAMPLE 5

The following illustrates the remarkable wet strengthening properties of wet strength pulp prepared from broke, according to the present invention.

The procedure of runs **2** and **6** of Example 4 are repeated, except that the time in run **2** in which the broke is in contact with the pulping medium is extended to 20 minutes, so that fiber liberation is complete, and the pulp is diluted to a consistency of only 0.6 percent.

The resulting pulps are used for the manufacture of paper by adjusting the pH to 6, forming the fibers into wet webs at 70 lb. basis weight in a laboratory handsheet machine, pressing the web between blotters and drying the resulting web on a laboratory drum drier having a drum temperature of 240° F.

The wet strengths of the resulting sheets are determined by the TAPPI method and are as follows:

Sheet No.	Pulping Temp. °F	Paper Wet Strength[1]
1	**75**	**8**
2	**175**	**3**

[1] Lb./inch

EXAMPLE 6

The following illustrates typical results achieved by variations in the temperature of the pulping medium, the pH of the medium, and the length of time during which the broke is in contact with the medium.

The procedure of Example 6 is repeated except that the pulping conditions are varied as is shown in the table below.

No.	Pulping conditions Temp. °F.	pH	Time mins.	Fiber liberation	Paper strength[2] Dry[1]	Wet[1]
1	77	5	70	Complete	Highest	Highest.
2	77	11	10	...do	Low	Low.
3	145	5	15	...do	High	High.
4	145	11	1	...do	Least	Least.

[1] Lb./inch.

[2] Comparative strength of paper made from the liberated fibers.

EXAMPLE 7

The following illustrates a large-scale application of the process of the invention to the pulping of a polyvinylamide glyoxal broke which possesses about maximum wet strength.

A charge of about 6 tons of mixed wet strength broke (trimmings and sliced substandard rolls) principally of towelling and napkin stock more than one week old of unbleached and bleached kraft and sulfite fibers containing 1.25 percent of a cationic polyvinylamide – glyoxal wet strength resin and having a basis weight of 8 lb. per 2,880 ft.^{2} is placed in a 20,000 gallon centrifugal pulper (Hydrapulper; cf U.S. Pat. No. 3,245,868) with sufficient water at 135° F. to provide consistency of 10 percent. The stirrer is started and the pH is adjusted to 9.5 by addition of aqueous sodium hydroxide. Pulping of the trim is very rapid.

Pulping of the rolls is complete in 15 minutes.

Paper made from the pulp thus obtained possesses about 50 percent of the wet strength of the paper of which the broke is composed.

EXAMPLE 8

The following shows on a comparative scale the wet strength effect of admixing the broke with virgin pulp with and without added polymer.

The procedure of Example 3 is repeated through the pulping step except that the starting broke is paper hand-sheets made by beater addition of 1 percent of the resin.

Aliquots of the pulp are taken.

One set of aliquots is processed into handsheets with addition of the cationic polyacrylamide-glyoxal polymer of Example 8 in amounts shown in the table below.

Another set of aliquots is processed in the same manner except that virgin pulp of the type of which the broke was composed is added in amounts shown in the table.

Results are as follows:

Run No.	Composition of Pulp, % Pulped Broke[1]	Virgin Pulp[2]	Polymer[3]	Strength[4] lb./in.
Con'l A[5]	None	None	None	3.90
Con'l B[6]	None	100	None	0.45
1	**100**	None	None	2.30
2	**100**	Do.	0.25	**3.35**
3	**100**	Do.	0.50	**3.85**
4	**100**	Do.	0.75	**4.15**
5	**100**	Do.	1.00	**4.35**
6	**50**	**50**	None	1.90
7	**50**	**50**	**0.25**	**2.75**
8	**50**	**50**	**0.50**	**3.05**
9	**50**	**50**	**0.75**	**3.90**
10	**50**	**50**	**1.00**	**4.05**
11	**25**	**75**	None	1.5
12	**25**	**75**	**0.25**	**2.25**
13	**25**	**75**	**0.50**	**3.45**
14	**25**	**75**	**0.75**	**3.75**
15	**25**	**75**	**1.0**	**3.80**
16	**10**	**90**	None	0.75
17	**10**	**90**	**0.25**	**2.65**
18	**10**	**90**	**0.50**	**3.35**
19	**10**	**90**	**0.75**	**3.50**
20	**10**	**90**	**1.0**	**3.45**

[1] Contains 1% polymer by weight (dry basis).

[2] % virgin pulp in pulp mixture.

[3] % polymer added to mixed pulp (polymer solids based on dry weight of fibers).

[4] Temporary.

[5] Starting broke (original handsheets).

[6] Paper made from virgin fibers. No polymer present.

The results show that the pulped broke of the present invention is strongly receptive to added increments of the polyvinylamide-glyoxal polymer, and that when absorbed on the fibers and the fibers are formed into a web and dried, the polymer exerts its normal or slightly better than normal wet strengthening effect.

EXAMPLE 10

The following illustrates the comparative effect of sodium hydroxide and sodium carbonate as pulping agents in the process of the present invention.

The procedure of Example 1 is repeated, except that the broke used has a basis weight such that its wet strength is 5.7 lb./inch. One sample of the broke is pulped at neutral pH (without addition of reagent as control), one is pulped with the pH adjusted to 10.0 by addition of sodium hydroxide and the third is pulped at pH 10.0 obtained by addition of sodium carbonate.

The resulting fibrous suspensions are remade into paper and the temporary (initial) wet strength of the paper is determined. Results are as follows:

	Pulping		Wet Strength lb./inch	
Sample	pH	Agent Used	Starting Broke	Remade Paper
Control	7.0	None	5.7	3.1
A	10.0	NaOH	5.7	1.7
B	10.0	Na_2CO_3	5.7	2.6

The results indicate that considerably less deterioration in the wet strengthening properties of the broke occurs when the pulping agent is sodium carbonate.

EXAMPLE 11

The process of the present invention finds application in the manufacture of wet strength paper, paper pulp having a uniform content of polyacrylamide-glyoxal polymer being employed as the wet strengthening agent in place of the polymer solution customarily employed, as follows.

Crude sulfite process pulp (bleached by the action first of oxygen under 20 lb./inch² pressure plus sodium hydroxide solution, washed, and then with sodium hypochlorite solution) is washed until substantially free of these agents. The pulp is then slurried in water at a consistency of 5 percent and at pH 8.5 to the slurry is added 1.5 percent (based on the dry weight of the fibers) of the water-soluble cationic thermosetting polyacrylamide-glyoxal resin used for the broke pulped in Example 1 is added as a 2 percent solution with gentle stirring for a few minutes to distribute the resin throughout the slurry. The resin is substantially, completely, and uniformly absorbed by the fibers within one minute. The fibers are recovered as a wet web, which is squeezed to 30 percent water content and stored two months to simulate expected aging.

The resulting web is readily slurried in water at pH 7 and 150° F. with moderate agitation in a Waring blender. The resulting slurry is mixed on equal quantity of virgin (resin-free) bleached sulfite pulp at 5 percent consistency. The resulting slurry is diluted to about 0.6 percent consistancy, beaten to a Canadian standard freeness of about 400 ml., and adjusted to pH 6. The fibers are made into paper in customary way, the wet web being dried on a drum drier having a surface temperature of 240° F. The resulting paper possesses about 80 percent of the wet strength which is imparted by the addition of 1.5 percent of the polymer to virgin bleached sulfite pulp. This wet strength is temporary and disappears after a few minutes contact with neutral water at room temperature, making the paper particularly suitable for the manufacture of paper towels and other paper intended for short-term use on the person.

EXAMPLE 12

The procedure of Example 9 is repeated except that the pulp is beaten to a Canadian standard freeness of about 400 ml. before addition of the polymer solution. The virgin pulp is simularly beaten, and subsequent beating is omitted. The wet strength of the paper is substantially the same and is similarly temporary.

We claim:

1. A method of pulping wet strength paper broke composed of water-laid cellulose fibers bonded together by an adsorbed content of a normally water-soluble thermosetting cationic wet strength polyvinylamide-glyoxal resin in thermoset state, which consists essentially in: contacting said broke in aqueous medium substantially free from oxidizing agent and having a pH between 5 and 10 and a temperature above 100° F. until the fiber-polymer bonds therein have loosened, and subjecting the broke to mechanical pulping until substantially all the fibers are liberated whereby a pulp is obtained composed of fibers having substantial wet strengthening properties.

2. A method according to claim 1 wherein the aqueous medium has a temperature above 100° F. and a pH above 9.

3. A method according to claim 1 wherein the contacting of the broke with aqueous medium and the mechanical pulping are performed simultaneously.

4. A method for the manufacture of wet strength paper, which consists essentially in forming an aqueous suspension of cellulose fibers pulped by a process according to claim 1, forming said fibers into a wet web without addition of wet strength resin thereto, and drying said web on rolls having a surface temperature between 190° F. and 250° F.

5. A process according to claim 4 wherein said polyvinylamide-glyoxal polymer is cationic, and a water-soluble cationic cellulose-substantive strengthening agent is added to said suspension before said fibers are formed into a web.

6. Papermaking pulp composed of water-laid cellulose fibers having a water content of 20 percent – 30 percent by weight and having a uniformly absorbed content of a water-soluble thermosetting ionic polyacrylamide-glyoxal resin in non-thermoset state as latent wet strengthening agent.

7. Pulp according to claim 6 the aqueous phase whereof has a pH in the range of 4 to 6.

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