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METHOD OF MAKING WET STRENGTH PAPER

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This invention relates to paper and to the method of making the same. More particularly, it relates to paper having improved properties and to the method of making the same.

In the manufacture of paper, the selected raw cellulosic material is subjected to cleansing, boiling, washing, bleaching and beating or reducing to pulp. The pulp comprises a dilute suspension of beaten cellulosic fibers, and paper is formed therefrom by draining most of the water therefrom and drying the resultant wet mat of entangled fibers until essentially water free. A commonly used process for sheeting the pulp comprises flowing the dilute suspension of beaten cellulose fibers onto a screen from which the water is drained, and thereafter passing the resulting wet mat of entangled fibers over and between drying rolls until essentially water free.

Paper made by the aforementioned process is known in the art as water-leaf paper. It quite readily absorbs water, possesses little or no strength when water wet, and has other properties which materially limit its use. In order to extend the field of use, various materials are commonly incorporated with the cellulose fibers either before or after the web or sheet is formed to produce or improve certain desirable properties. For example, rosin or animal glue have been employed to impart water resistance, clay to improve printing properties, plasticizers to enhance softness, and starch to improve the dry strength of the paper. Such papers, however, do not have a high wet strength, which is highly desirable for a number of various uses.

Paper has also been coated with various water resisting compositions. Due to the coating, the water absorbency of the paper has been reduced to a minimum and the product has a different appearance, feel and "hand" from uncoated papers.

Many attempts have been made to produce paper having high wet strength and high water absorbency. One procedure proposed treating paper with viscose. In such a process the viscose was impregnated into the paper and thereafter converted into regenerated cellulose. Due to the use of viscose, an odor was imparted to the paper and frequently the paper was discolored. The removal of the odor and the discoloration required deodorizing and bleaching operations, which made the process expensive.

An object of this invention is to provide a new

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and improved paper and method of preparing the same.

Another object of this invention is to provide a paper having improved tensile strength and bursting strength both in the dry and in the water wet state.

A further object of this invention is to provide a paper wherein the resistance of the paper to linting and to rubbing or abrasion, either in the dry or water wet state, is improved.

A specific object of this invention is to provide a highly absorptive paper having improved tensile strength both in the dry and water wet condition.

Other and additional objects will become apparent hereinafter.

The above objects are accomplished, in general, by impregnating paper with a liquid composition containing a synthetic linear polyamide and formaldehyde and drying said paper in the presence of an acid, the quantity of the latter being such as will not degrade the cellulose fibers. After drying, the dried paper is washed with water until substantially acid free and the paper redried.

The exact nature of the chemical changes or reactions, if any, taking place during the process are not definitely known. Irrespective of the changes or reactions which take place during the process, the product of this invention does not materially differ in appearance and feel from the untreated paper and is characterized by a high water absorbency and high tensile strength. As will hereafter appear, the tensile strength, especially in the water wet state, has been improved to such a degree over the untreated paper that the results are truly amazing.

In the preferred process, the synthetic linear polyamide and formaldehyde are dissolved in an appropriate solvent to which the acid is added and water-leaf paper impregnated with such solution. After impregnation, the paper is dried at an elevated temperature. The dried paper is then washed in water until acid free and then redried.

The details and manner of practicing the invention will become apparent by reference to the following specific examples, it being understood that these examples are merely illustrative embodiments of the invention and that the scope of the invention is not limited thereto. Throughout the examples, the proportions are parts by weight unless otherwise specified.

EXAMPLE I

Water-leaf paper with a base weight of 10 lbs. per 17 x 22—500 ream was dipped into a bath consisting of

	Parts
Self-polymerized omega amino caproic acid	1.25
Formic acid (95%)	88.75
Formaldehyde (37%)	10.00

The bath was prepared by first dissolving the polymerized omega amino caproic acid in the formic acid and thereafter adding the formaldehyde.

Upon removal of the paper from the treating bath, the excess liquid was removed by blotting between blotting paper. The paper was then dried for 30 seconds on the surface of a glass cylinder containing steam at 100° C. The paper was then washed in water until acid free and then redried on the surface of the glass cylinder for 30 seconds.

The treated paper contained 1.4% by weight of polymerized omega amino caproic acid.

The paper resulting from this process did not materially differ in appearance and feel from the untreated paper but was characterized by high tensile strength and high water absorptivity.

The nature of the improvement of the treated paper of this example over the untreated paper is shown by the following table comparing the physical properties of the untreated and treated paper:

Table I

	Dry Tensile, kg./15 mm.		Wet Tensile, kg./15 mm.		Dry Tear Strength, g./sheet		Rate of Climb of Water, secs. per in.	
	M. D.[1]	C. D.[2]	M. D.	C. D.	M. D.	C. D.	M. D.	C. D.
Untreated Paper	2.19	0.91	0.02	0.02	54	67	26	29
Treated Paper	4.09	2.05	1.84	0.74	32	41	28	41

[1] M. D. refers to the physical tests made in the machine direction of the paper, i. e. parallel to the direction in which the paper passed through the paper machine during its manufacture.
[2] C. D. refers to the physical tests made in the cross-machine direction, i. e. at right angles to the machine direction of the paper.

The rate of climb of water is the test used to determine the water absorption. The test consists of vertically suspending and immersing 1" of a test strip of paper 1" wide in distilled water at a controlled temperature of 75° F. The water then penetrates up the paper by capillary attraction. The measurement consists in determining the time, in seconds, for the water to climb 1".

EXAMPLE II

Water-leaf paper of the type referred to in Example I was dipped into the following bath and treated as set forth in Example I:

	Parts
Self-polymerized omega amino caproic acid	1
Oxalic acid	4
Ethyl alcohol	93
Formalin (37%)	2

The bath was prepared by first dissolving the self-polymerized omega amino caproic acid and the oxalic acid in the ethyl alcohol, and thereafter the formalin was added.

Paper produced in accordance with this example contained 1.3% of self-polymerized omega amino caproic acid.

Paper resulting from this example possessed properties similar to those of Example I.

EXAMPLE III

The following bath was applied to water-leaf paper by a laboratory size press and the treated paper was dried for 30 seconds on a glass cylinder containing steam at 100° C.:

	Parts
Self-polymerized omega amino caproic acid	1
Oxalic acid	4
Ethyl alcohol	75
Formalin (37%)	20

The treating bath was prepared by dissolving the polyamide and oxalic acid in a mixture of the alcohol and formalin.

After the paper was dried as previously described, it was washed until essentially acid free and redried on the surface of the glass cylinder for 30 seconds.

The treated paper contained 0.95% of synthetic linear polyamide.

The paper resulting from this example was highly water absorptive and had a relatively high wet tensile strength as well as a relatively high dry tensile strength.

EXAMPLE IV

Size-free paper was immersed in the following bath for 5 minutes:

	Parts
Self-polymerized omega amino caproic acid	2
Ethyl alcohol	79
Water	79
Formaldehyde (37%)	40

In this treating bath, the self-polymerized omega amino caproic acid existed essentially as small colloidally dispersed particles. The bath was prepared by dissolving the self-polymerized omega amino caproic acid in the alcohol and 19 parts of water and the resulting solution added to a mixture of 60 parts of water and the formaldehyde whereby the self-polymerized omega amino caproic acid was precipitated.

After the removal of the paper from the bath, it was pressed between sheets of blotter paper to remove excess liquid. The paper was then partially dried by placing on a drier at 100° C. for approximately 15 seconds. The paper was then acidified by immersion in a mixture containing 50 parts of 95% formic acid and 50 parts of water. The excess acid was removed by blotting and the paper was dried for 30 seconds at 100° C. Thereafter, it was washed until essentially acid free and redried at 100° C.

The specific examples disclose the use of specific synthetic linear polyamides. It is to be understood, however, that the invention is not restricted to such specific synthetic linear polyamides. In general, synthetic linear polyamides derived from polymerizable mono amino carboxylic acids or their amide-forming derivatives

and those derived from the reaction of suitable diamines with suitable dicarboxylic acids or amide-forming derivatives of dibasic carboxylic acids, as disclosed in United States Patents Nos. 2,071,250, 2,071,253, 2,130,523 and 2,130,948, can be used.

Polymerized 6-amino caproic acid, polymerized 9-amino nonanoic acid, polymerized 11-amino undecanoic acid, polyhexamethylene adipamide and polyhexamethylene sebacamide are additional illustrative specific examples of synthetic linear polyamides which can be used in this invention.

Though as shown by the examples formaldehyde is preferred, it is to be understood that the invention is not restricted thereto since formaldehyde derivatives, such as paraformaldehyde, hexamethylene tetramine and dimethylol urea, can also be used.

In the processes described in the examples, the paper subsequently to impregnation with the treating bath was dried in the presence of an acid, such as oxalic or formic. In addition to these acids, other organic acids, such as, for example, acetic, can be used. Likewise, inorganic acids, such as sulfuric, hydrochloric and phosphoric, can be employed. In all cases, the greater the quantity of acid present during the drying operation, the more effective is the process. However, the quantity of the acid in no case should be such that acid degradation of the fibers becomes substantial.

The process as shown by Example IV can be successfully carried out by first incorporating the synthetic linear polyamide and the formaldehyde in the paper and thereafter in another operation incorporating the requisite quantity of acid. However, in the preferred embodiment of the invention, the three ingredients are simultaneously incorporated into the paper by one operation by impregnation with a liquid composition containing them. If, as shown in Example I, the acid (formic) is a solvent for the synthetic linear polyamide, it, the acid, can constitute the liquid vehicle of the composition. When the acid component is not a solvent for the synthetic linear polyamide, then a solvent for the polyamide, which is preferably also miscible with the formaldehyde and acid (or, in the event the acid is a solid, the latter will be soluble in the solvent), is utilized.

As shown by Examples II and III, wherein an ethyl alcohol soluble synthetic linear polyamide, oxalic acid (to provide the necessary acidity during drying) and formaldehyde are utilized, they can be simultaneously incorporated in paper from a (single) ethyl alcohol treating bath by a single operation. Other solvents in place of ethyl alcohol, as will be apparent to one skilled in the art, can be used.

In the examples, the approximate ratio of mols of formaldehyde to base mols of polyamide is as follows:

Example I	11:1
Example II	1.5:1
Example III	28:1
Example IV	28:1

Herein the term "base mol" designates the molecular weight of the monomer unit is distinguished from the molecular weight of the long chain polymer (polyamide) molecules. It is, however, to be understood that the relative proportions of the synthetic linear polyamide and the formaldehyde, or its equivalent, are not limited to those set forth in the specific examples. However, the preferred relative proportions of the

polyamide and formaldehyde, or its equivalent, with water-leaf paper is in the ratio of 1 base mol or polyamide to from 1 to 15 mols of formaldehyde, since such proportions produce the most desirable results. When the impregnating bath also contains the acid, the latter is present in an amount of from ¼% to 7% by weight of the bath.

The temperature to which the impregnated paper is subjected is not critical. Good improvement in wet and dry tensile strength with minimum reduction in water absorptiveness has been obtained by air drying the impregnated paper overnight at room temperature (25° C.). Drying the impregnated paper for 60 seconds at 118° C. (a representative temperature for paper machine driers) also produced very good improvement. Thus, in general, the improvements obtained by this invention are attained irrespective of the mode or manner of drying. The selected temperature and time of drying should be such that the degradation of the cellulose fibers does not become substantial.

The improvement in physical characteristics of (dried) water-leaf paper treated by the instant invention is obtained in conjunction with a minimum reduction in the absorptivity of the untreated paper. As hereinbefore shown, not only is the dry tensile strength improved, but also the wet tensile strength is substantially improved. The improvements in the physical properties are obtained through the conjoint use of the synthetic linear polyamide and the formaldehyde or derivatives thereof. The improvements obtained from the conjoint use of the synthetic linear polyamide and the formaldehyde or derivative thereof are not the additive improvements of the properties of these components, but, as hereinbefore described, unexpected and surprising improvements are obtained. That the improvements are not merely the summation of the properties of the synthetic linear polyamide and formaldehyde are shown by the following table wherein the physical properties of water-leaf paper similarly treated with the respective compositions set forth are given:

Table II

Bath	Per Cent Polyamide in paper	Dry Tensile		Wet Tensile	
		M. D.	C. D.	M. D.	C. D.
I	1.3	3.85	2.25	2.66	1.18
II	2.0	3.19	1.65	0.08	0.06
III	0.0	2.24	1.41	0.71	0.49

The compositions of baths I, II and III of the above Table II are as follows:

	Bath I	Bath II	Bath III
Self-polymerized omega amino caproic acid, parts by weight	1	1	0
Formalin (37% formaldehyde), parts by weight	20	0	20
Oxalic acid, parts by weight	4	0	4
Ethyl alcohol, parts by weight	75	99	76
Total	100	100	100

The desired properties are obtained when the treated paper contains from 1.2% to 1.5% by weight of the synthetic linear polyamide. However, decided improvements are obtained when the treated paper contains the synthetic linear

polyamide in an amount as low as 0.5% or as high as 5.0% by weight of the paper.

Though in the previous embodiments the paper was impregnated with a bath containing the synthetic linear polyamide and formaldehyde or its equivalent and the impregnated paper dried in the presence of an acid, the latter being either a component of the impregnating bath or applied to the impregnated paper, the invention is not restricted to such procedures and such specific impregnating baths. An impregnating bath obtained by dissolving in an appropriate solvent the product separated from the reaction mixture resulting from heating a solution of a synthetic linear polyamide of the type previously described in an appropriate solvent with formaldehyde, or its equivalent, in the presence of an acid of the type hereinbefore described can also be used. In preparing such a bath, a solution of a synthetic linear polyamide of the type hereinbefore described, and preferably self-polymerized amino caproic acid in ethyl alcohol, is heated with formaldehyde under acidic conditions to 60° C. to 70° C. for approximately ½ to 1 hour, the proportions of the ingredients being as hereinbefore described. Thereafter, the reaction product is precipitated into a non-solvent, such as acetone. This precipitate, which is in the finely divided state, is washed with water and, after dissolving in ethyl alcohol, constitutes the impregnating bath. Paper, and particularly water-leaf paper, is impregnated with such bath and, after the excess solution is removed, the impregnated paper is dried under acidic conditions for approximately 30 seconds on a glass cylinder containing steam at 100° C. If desired, the acid may be incorporated in the impregnating bath or added to the impregnated paper in a manner similar to that previously described.

An illustrative example of an impregnating bath utilizing the reaction product is as follows:

	Parts by weight
Reaction product (2.2 mols of formaldehyde and 1 base mol of self-polymerized omega amino caproic acid)	2
Oxalic acid	4
Ethyl alcohol	94

Herein the expression "composition containing the polyamide and formaldehyde," or its equivalent, is, unless otherwise specified, intended to cover the initial impregnating composition wherein such components exist as such or have been preliminarily reacted as herein described.

The invention is not restricted to any precise mode of incorporating the desired components in the paper. In general, any method for incorporating the ingredients substantially homogeneously in the paper, such as, for example, impregnation, dipping, flowing, spraying, etc., can be used.

The instant invention provides a highly absorbent paper which is characterized not only by a high dry tensile strength but also by a remarkably high wet tensile strength. The treated paper of this invention is admirably suited for use as paper toweling, filter paper, label paper, handkerchiefs, napkins, diapers, etc. and, in general, for any purpose wherein a high wet strength is prerequisite.

As is apparent from the preceding disclosure, the invention is admirably suitable for use in the treatment of (dried) water-leaf paper. However, the invention is not restricted to such paper. Since it can be applied to various other types of papers, the improvement imparted to such papers depends on the nature of the paper treated.

Since it is obvious that various changes and modifications may be made in the above description without departing from the nature or spirit thereof, this invention is not restricted thereto except as set forth in the appended claims.

I claim:

1. In a method of preparing absorptive paper of high wet strength from water-leaf paper without materially changing the appearance and feel thereof, which comprises impregnating water-leaf paper with a solution comprising 1 base mol of self-polymerized omega amino caproic acid and 1 to 28 mols of formaldehyde, said self-polymerized omega amino caproic acid being present in said solution in an amount of from 1% to 1.25% by weight, drying said paper in the presence of an acid catalyst, removing said acid catalyst, and redrying the resulting product whereby said paper is substantially uniformly impregnated throughout with from 1.2% to 1.5% of said polymerized omega amino caproic acid.

2. In a method of preparing absorptive paper of high wet strength from water-leaf paper without materially changing the appearance and feel thereof, which comprises impregnating water-leaf paper with a solution comprising 1 base mol of self-polymerized omega amino caproic acid and 1 to 28 mols of formaldehyde dissolved in ethyl alcohol, said solution containing an acid catalyst, said self-polymerized omega amino caproic acid being present in said solution in an amount of from 1% to 1.25% by weight, drying said paper, removing said acid catalyst, and redrying the resulting product whereby said paper is substantially uniformly impregnated throughout with from 1.2% to 1.5% of said polymerized omega amino caproic acid.

3. In a method of preparing absorptive paper of high wet strength from water-leaf paper without materially changing the appearance and feel thereof, which comprises impregnating water-leaf paper with a solution comprising the following ingredients in the proportions named:

	Parts by weight
Self-polymerized omega amino caproic acid	1
Oxalic acid	4
Ethyl alcohol	93
Formalin (37%)	2

drying said paper in the presence of the oxalic acid, removing said oxalic acid, and redrying the resulting product whereby said paper is substantially uniformly impregnated throughout with about 1.3% of said polymerized omega amino caproic acid.

4. In a method of preparing absorptive paper of high wet strength from water-leaf paper without materially changing the appearance and feel thereof, which comprises impregnating water-leaf paper with a solution comprising the following ingredients in the proportions named:

	Parts by weight
Self-polymerized omega amino caproic acid	1
Oxalic acid	4
Ethyl alcohol	75
Formalin (37%)	20

drying said paper in the presence of the oxalic acid, removing said oxalic acid, and redrying the resulting product whereby said paper is substantially uniformly impregnated throughout with about 0.95% of said polymerized omega amino caproic acid.

5. In a method of preparing absorptive paper of high wet strength without materially changing the appearance and feel thereof, the improvement which comprises impregnating paper with a solution of formaldehyde containing about 1 per cent of a synthetic linear polyamide which consists of the polymerization product of a linear polymer-forming material selected from one of the groups consisting of monoaminocarboxylic acids and mixtures of diamine with dibasic carboxylic acid, and drying said paper after impregnation in the presence of an acid catalyst whereby said paper is substantially uniformly impregnated throughout with from 0.5% to 5.0% of said synthetic linear polyamide resin.

6. In a method of preparing absorptive paper of high wet strength without materially changing the appearance and feel thereof, the improvement which comprises impregnating paper with an acidic solution of formaldehyde containing an acid catalyst and about 1 per cent of a synthetic linear polyamide which consists of the polymerization product of a linear polymer-forming material selected from one of the groups consisting of monoaminocarboxylic acids and mixtures of diamine with dibasic carboxylic acid, drying said impregnated paper, washing said dried paper with water to remove the acid catalyst and redrying said washed paper whereby said paper is substantially uniformly impregnated throughout with from 0.5% to 5.0% of said synthetic linear polyamide resin.

7. The method of preparing a highly absorptive paper of improved tensile strength both in dry and water wet condition, which comprises impregnating paper with a formic acid solution containing formaldehyde and about 1 per cent of self-polymerized omega amino caproic acid, drying the impregnated paper, washing the dried paper with water and redrying the paper whereby said paper is substantially uniformly impregnated throughout with from 0.5% to 5.0% of said polymerized omega amino caproic acid.

8. In a method of preparing absorptive paper of high wet strength from water leaf paper without materially changing the appearance and feel thereof, which comprises impregnating water leaf paper with a solution comprising the following ingredients in the proportions named:

	Parts by weight
Self-polymerized omega amino caproic acid	1.25
Formic acid (95%)	88.75
Formaldehyde (37%)	10.00

drying said paper in the presence of the formic acid, removing said formic acid and redrying the resultant product whereby said paper is substantially uniformly impregnated throughout with about 1.4% of said polymerized omega amino caproic acid.

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