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PROCESS FOR IMPROVING THE WET STRENGTH OF PRODUCTS OBTAINED FROM CELLULOSIC PULP

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The present invention deals with the treatment of paper, cardboard and different products and articles made from cellulosic pulp, with the view of giving them properties which are not natural to them.

The above description "cellulosic pulp" is intended to convey pulp for paper, cardboard and other articles containing a cellulosic substance or having a cellulosic nature, as for example, those obtained from agave, alfa-grass, cane-trash, bamboo, sea-weed, coniferous wood, wood in general, hemp, Manila hemp, rags, mulberry wood, esparto-grass, jute, linen, palm, reeds, sorghum, etc.

These pulps may be crude or refined. They can be obtained by chemical processes or by any other means and can contain fillers, size, glue, colouring matter, or any other kind of modifier. In order to simplify the description of this invention, the term "paper" only is used.

In any case it is to be understood that this term "paper" as used herein includes cardboard, paper pulp, or pulp of a general cellulosic nature, as specified above, also any article, object or product obtained from or manufactured with these substances. One of the characteristics of paper, which is a very serious drawback for certain uses, is that of having a very limited resistance to water, liquid and vapor, as the fibres with which it is composed swell and the bonds binding the fibres together destroyed. Thus the paper speedily becomes useless when wet and tends to disintegrate and become again the formless pulp it was originally.

Apart from this, the prolonged action of humidity encourages the formation of mildew, which damages its quality and tends to decompose it.

These and still other disadvantages greatly limit the use of paper in various spheres of human activity.

With the aim of giving paper and cellulose substances greater resistance to humidity and water, there has been recommended, among other things, the addition of methylolureas and their derivatives, alkyl-ethers. However it has been established that ureas of this kind generally render the paper rigid and crackable, as the resin gives its own characteristics to paper thus treated.

The present invention deals with a process intended to solve or reduce these inconveniences and aims at obtaining paper having a remarkable resistance to humidity, water and aqueous liquids and also to the action of mildew.

It is now possible, by this process, to obtain paper having these qualities, while still remaining quite flexible, resisting increasing wear and tear, which has a normal aspect and can keep good absorption and permeability to water and liquids in general, and also good permeability to gases.

Paper obtained by the use of this process can find countless uses in unexpected branches of industrial, commercial or scientific activity.

The present invention can be applied to the preparation or manufacture of a great many paper articles, which are resistant to water, such as the following examples,

which are not limitative: towels, bath-mats, hand-towels, handkerchiefs, tablecloths, linen, table napkins, diapers, sponges, furniture polishers, dusters, floorcloths, underarm protectors, string and rope, sanitary objects, sanitary paper, tea-cloths, paper filters, cardboard filters, bags, cardboard boxes, corrugated cardboard, objects moulded from paper pulp, cellulose wadding, posters, notice boards, all kinds of packing material, boxes, receptacles, paper for covering or containing fruit, vegetables, fish, shellfish, flowers, meat and in general all substances preserved in liquid or damp surroundings.

Papers and documents subjected to wear and tear can also be prepared or treated according to the invention, as for example: maps, identity cards, road or geographical maps, engravings, books of art, cheques, bonds, bank-notes, photographic paper, tracing, drawing or painting paper, paper for decoration and ornaments, wall papers, book-binding paper etc. and in general all articles or products with a paper basis, where resistance to water, weather, wear and tear, and also to certain chemical agents, is required.

The process forming the object of this invention is chiefly characterized by the following points:

(1) That the paper is treated:
- (*a*) by polyureas hydroxymethylated on the nitrogen of ureido nature, and/or
- (*b*) by polyureas alkoxymethylated on the nitrogen of ureido nature;

(2) That the N-hydroxymethylated or N-alkoxymethylated polyureas are made to react on the cellulose matter composing the paper, to condense it with the latter, in order to modify its composition and characteristics.

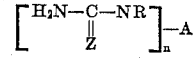
For the ends of the present invention it should be understood in the present description:

For N-hydroxymethylated polyureas, the polyureas in which the reactive hydrogen linked to the ureido nitrogen has been, partly or entirely, replaced by hydroxymethyl groups;

In the same way for N-alkoxymethylated polyureas, there is encompassed either the derivatives of these N-hydroxymethylated polyureas, of which one or more of the N-hydroxymethylated groups have the hydroxylic hydrogen replaced by an alkyl radical, or, also, the polyureas having only N-alkoxymethylated groups.

The alkyl radical can, for example, preferably represent methoxy or ethoxy, or such other radicals as propoxy, butoxy etc.

The N-hydroxymethylated and N-alkoxymethylated polyureas are obtained starting from polyureas which correspond to the general formula indicated below and in which the ureido groups are separated by at least two carbon atoms:



where

A represents a substituted or unsubstituted acyclic or cyclic hydrocarbon radical which may be interrupted by oxygen, sulfur or nitrogen atoms, A having a valency equal to the value of *n*,

Z represents oxygen or sulphur;

n represents an integer number, equal or superior to two.

R is selected from the group consisting of hydrogen and organic radicals which, with N in the formula, form an integral part of the polyvalent radical A.

The acyclic polyvalent radicals A may be derived from:

(*a*) unsubstituted saturated linear hydrocarbon chains containing from 2 to 12 carbon atoms;

(*b*) saturated hydrocarbon chain containing from 2 to

18 carbon atoms and substituted by hydroxyl, amine, alkoxy, carboxy or acyl groups;

(*c*) saturated hydrocarbon chains interrupted by nitrogen and oxygen atoms and which may be substituted by halogen or hydroxyl, alkoxy, acyl, carboxy, or amino groups;

(*d*) saturated hydrocarbon chains interrupted by nitrogen and containing from 4 to 60 carbon atoms, and which may be substituted by halogen, or by hydroxy, amino, alkoxy or acyl groups;

(*e*) saturated hydrocarbon chains interrupted by oxygen;

(*f*) saturated hydrocarbon chains interrupted by sulfur atoms.

The cyclic polyvalent radicals represented by A in the the general formula may be derived from, e.g.,

(*a*) cyclohexane, dimethyl cyclohexane, benzene, methylbenzene, dimethylbenzene, cyclopentane, hexahydropyrazine, etc.

Some examples of polyureas corresponding to the general formula, which are not limitative and by means of which the derivatives N-hydroxymethylated and/or N-alkoxymethylated can be obtained, the use of which characterizes the invention, are here given:

Diureido-1,2 ethane; diureido-1,3 propane; diureido-1,4 butane; diureido-1,5 pentane; dieureido-1,7 hexane; diureido-1,6 heptane; diureido-1,8 octane; diureido-1,9 nonane; diureido-1,10 decane; diureido-1,11 undecane; diureido-1,12 dodecane; diureido-1,16 hexadecane; diureido-1,6 methoxy-3 hexane; diureido-1,9 methyl-5 nonane; diureido-1,5 (carbamyl-3 aza-3 tetracarbane); diureido-1,8 (dicarbamyl-3,6 diaza-3,6 hexacarbane); diureido-1,11 (tricarbamyl-3,6,9 triaza-3,6,9 octacarbane); diureido-1,13 (carbamyl-7 aza-7 dodecacarbane); ureido-1 (hydroxy-2-ethyl)-1-(ureido-2-ethyl)-1-urea; triureido-1,3,5 heptane; triureido-1,4,6 hexane; tetrureido neopentane; dithioureido-1,2 ethane; dithioureido-1,3 propane; diureido-1,4 benzene; diureido-alpha,4 toluene; diureido-1,4 cyclohexane; dicarbamyl-1,4 hexahydropyrazine; diureido-2,2′ diethyl ether; diureido-3,3′ dipropyl ether; diureido-4,4′ dibutyl ether; diureido-2,2′ diethyl sulfide; diureido-3,3′ dipropyl sulfide; etc.

The polyureas hydroxymethylated on the nitrogen of ureido nature, derived from polyureas corresponding to the general formula mentioned above, are obtained by causing these polyureas to react preferably in the presence of an alkaline catalyzer with methanal, at the rate of a molecule of the latter for each hydroxymethyl group to be formed, by substituting a reactive hydrogen linked to the nitrogen. The catalyzers which can be employed in this reaction are, for example: calcium hydroxide, barium hydroxide, sodium hydroxide etc.

For the ends of this invention, the quantity of methanal which can be used for each polyurea, may be varied within large enough limits, which, for example, can go from a methanal molecule for each ureido group to a molecule for each reactive hydrogen linked to the nitrogen atoms present in the polyurea molecule. Greater quantities than those mentioned may also be used. The methanal may be used in a solution of water or alcohol and it can also be replaced by its polymers or any other substance which can liberate it, such as, for example, paraformaldehyde, trioxane, hexamethylene-tetramine etc.

The nitrogen ureido alkoxymethylated polyureas are obtained preferably by causing the N-hydroxymethylated polyureas to react with an alcohol in the presence of a catalyzer of acidic nature, as, for example, phosphoric acid, chlorhydric acid, sulphuric acid, sodium sulfate acid, sodium phosphate acid, oxalic acid, citric acid, etc.

Alcohols susceptible of being used to obtain these ethers may be of different types, saturated or not. Alkanols are preferred, particularly methanol and ethanol. Amongst the N-alkoxylated polyureas those having N-methoxymethyl or N-ethoxymethyl groups are more suitable for the accomplishment of the invention.

In a general way, reactions for obtaining N-hydroxymethylated or N-alkoxymethylated polyureas, can be realized with the aid of substances having a dissolving or dispersing action on the reacting or resulting products.

N-hydroxymethylated or N-alkoxymethylated polyureas, whose use is the object of the invention, are characterized by great reactive power and appear particularly appropriate for giving better quality and new properties to paper.

The action which determines this transformation of the quality and properties of paper should not only be looked for in the simple resinifying of these polyureas on the fibres, but also in the possibility that these N-hydroxymethylated or N-alkoxymethylated polyures have, according to all evidence, in order to react, to combine themselves or condense with the lignins, the celluloses, or other constituents of the cellulose fibre walls, to form bonds with, for example, the hydroxyl groups of the cellulose of ether-oxide nature, or other bridging bonds between the macromolecules composing the fibres.

The formation of intermolecular bridges, which modify the structure of the original fibres, contributes greatly to giving them new qualities and properties.

A characteristic of the present invention consists in causing the celluloses of the paper to react with the N-hydroxymethylated or N-alkoxymethylated polyureas, in order, as has been said, to modify thus their natural properties and give them new qualities.

This operation should be performed, preferably, under the action of heat, for a variable period according to the products brought into action and the results desired. This should be done, preferably, in the presence of a catalyzer of an acid nature.

The N-hydroxymethylated and N-alkoxymethylated polyureas should, preferably, be used in a monomer or monomolecular condition.

However, these polyureas could also be used in a most complex structural condition, for example, that resulting from the linking up of two or more of the said monomers, either by means of ether-oxide bonds coming from the dehydration of hydroxymethyl functions, or by coupling by means of methylenic bonds, etc. In a general way, those having a structure slightly condensed, still having active power and being capable of ulterior reaction, can be used. The crude products resulting from reactions destined to obtain N-hydroxymethylated or N-alkoxymethylated polyureas can also be used to realize the present invention; their use is therefore included in this, even if there is a surplus of products used for the reactions present.

N-hydroxymethylated or N-alkoxymethylated polyureas can also be used mixed together, in the same way their obtainment can be foreseen, even in the presence of the paper.

N-hydroxymethylated and N-alkoxymethylated polyureas, should, preferably, be employed in a dissolved, dispersed or emulsified condition, according to convenience or necessity. Any product capable of dissolving, dispersing or emulsifying may be used. In general, the N-hydroxymethylated or N-alkoxymethylated polyurea is applied in aqueous or aqueous-alcoholic medium at a pH between 4.5 and 6.5, the article is dried, and then heated until the condensate with the cellulose of the article is formed.

The N-hydroxymethylated and N-alkoxymethylated polyureas with which this invention deals can be used by themselves or together with other products susceptible of reacting, or not, to form with them, for example, mixed condensations. Urea, thiourea and their methylol derivatives, melamines, hydroxymethylamides and hydroxymethylpolyamides, amines, phenolic products, resins and polymers of various kinds, plastifyers etc. for example, can be used to this end. To accomplish the invention, the

quantities of N-hydroxymethylated or N-alkoxymethylated polyureas which can be used, according to the dry weight of the paper, vary within large enough limits, according to their properties and the results desired, also the nature, composition and structure of the cellulosic substances treated.

Generally speaking, quantities between 1% and 6% of the dry weight of these substances give the best results. However, in certain cases reduced quantities can be used, such as 0.25% of the dry weight, or greater quantities like 12%. The principal aim of the present invention is that of giving a remarkable mechanical resistance to paper when brought into contact with water, without materially changing either its appearance, pliability, porosity and fell, or its power of absorbing water and inks.

For these reasons, its accomplishment with N-hydroxymethylated and N-alkoxymethylated polyureas, used in small quantities, in proportion to the weight of the dry paper treated, is preferable.

The aim of the present invention is not that of coating or impregnating the paper with large proportions of the resins obtained by the condensation of these polyureas, as these resins would, in that case, modify its aspect and pliability and render it rigid, at the same time diminish its power of absorbing water and inks, by giving it, as is evident, their own characteristics.

To give the paper greater water resistance, as well as other properties envisaged in the invention, it is imbibed by spraying, soaking, inking, or any other means, with solutions, suspensions or emulsions of the N-hydroxymethylated or N-alkoxymethylated polyureas indicated, preferably in the presence of a catalyzer of acidic nature.

For example, paper thus treated is passed between two compressor rollers, or else squeezed, to remove any excess of the product absorbed and to obtain a homogeneous impregnation.

The paper is then dried in an appropriate for instance progressive manner, at a temperature not exceeding, for example, 50° C., in order to avoid complete reaction or condensation of the N-hydroxymethylated and N-alkoxymethylated polyureas while it is still wet.

The paper is then submitted to a higher temperature, in general between 80° C. and the critical temeprature of the cellulose, for example, at 125° C., and this for a length of time in inverse proportion to the temperature. This exposal to heat can thus last from some seconds to several minutes. The paper can also be submitted to a temperature below 80° C. during a period which can last, according to the products being used, from some hours to several weeks.

In the latter case a large dose of catalyzer may generally be useful.

Another appropriate method of accomplishing the invention consists in the addition of sufficient quantities of the N-hydroxymethylated or N-alkoxymethylated polyureas, mentioned above, directly into the container holding the paper pulp, incidentally, together with the catalyzers chosen.

The sheets of paper, or other articles which are manufactured with the pulp thus treated, are submitted after drying, to heat treatment, within the limits of temperature mentioned above and for a period of time corresponding to the latter.

This extremely practical method of working allows paper, having a greater resistance to humidity, to be obtained very simply.

As has been stated, the presence of condensation catalyzer agents also has its importance on the results obtained.

Non-limitative examples of substances having these properties are cited as follows: mineral acids, such as chlorhydric acid, sulphuric acid, nitric acid, phosphoric acid, tungstic acid, etc.; organic acids, such as, chloracetic acid, oxalic acid, maleic acid, succinic acid, adipic acid, glycolic acid, lactic acid, citric acid, etc. salts, such as, ammonium chloride, zinc chloride, aluminium chloride, sodium acid sulfate, ammonium sulfates, ammonium nitrate, ammonium phosphates, etc. The quantities of catalyzer agents to be employed with the N-hydroxymethylated and N-alkoxymethylated polyureas depends on the speed of reaction desired, their activity, the kind of substance treated, the temperatures at which the operation is performed, etc.

Quantities of catalyzers from one percent to five percent of the weight of the N-hydroxymethylated or N-alkoxymethylated polyureas are, according to the invention, generally suitable.

Below are given some particular examples of the application of the invention in practice.

These typical examples are, however, only given as a guide and not as limiting the invention to the particulars and details given, this also applies to the preparation of the N-hydroxymethylated and/or N-alkoxymethylated polyuraes, whose use characteristics the invention. The latter, on the contrary, covers all the numerous modifications and variations that can be brought within its scope, which is vast enough and clearly defined in the present description.

EXAMPLE NO. 1

A mixture of 70 parts by weight of diureido-1,6 hexane and 130 parts by weight of a 37% neutralized aqueous solution of methanal, is heated until the diureido-1,6 hexane is dissolved.

Then the temperature is allowed to go down to 25° C. and by means of a 5% solution of caustic soda, the pH of the mixture is brought to about 8.5.

The preparation is heated for one hour between 40° and 60° C. and the pH is maintained within the limits of 8 and 8.5.

Then the temperature is again brought down to around 20° C. and the pH is reduced to 7.2 by means of diluted chlorhydric acid. The water present is evaporated, preferably under reduced pressure at temperatures not exceeding 50° C.

The residue consists chiefly of diureido-1,6 hexane N-hydroxymethyl.

Then 0.8 part by weight of this residue are removed and a little warm water is added to them in order to hasten dispersion and solubility.

The weight of water is then made up to 100 parts.

Following this 0.02 part by weight of adipic acid are added.

The sheets of paper are immersed in this bath and left in it until completely saturated. All excess liquid is removed from the surface of these sheets and they are dried at 40° C. Then they are submitted to a temperature of 120° C. for 80 seconds.

Sheets thus treated, when brought into contact with water, show an extraordinary resistance. Thus sheets of paper weighing 20 gms. to the square meter, treated as above, still reveal a very remarkable resistance, even after more than 40 days immersion in water.

EXAMPLE NO. 2

30 parts by weight of the vacuum dried product obtained in Example No. 1 and consisting chiefly of diureido-1,6 hexane N-hydroxymethylated are dissolved in 80 parts of manthanol.

The temperature of the mixture is brought to around 10° and at this moment, little by little, an alcoholic solution of phosphoric acid is added, while continually stirring, until an acidity corresponding to about pH 2.5 is obtained.

The acidified liquid is maintained at room temperature for 40–50 minutes or more, care being taken to avoid resinification. It is then neutralized with diluted caustic soda and, if desired, the alcohol which has not reacted is evaporated, preferably under reduced pressure. The

crude product obtained contains diureido-1,6 hexane N-methoxymethylated.

After elimination of excess alcohol, 3 parts of this crude product are dissolved in 50 volumes of methyl alcohol and completed with water to a total of 100 parts by weight. Phosphoric acid is added to this mixture to bring it to pH 5.5.

Sheets of tissue paper, weighing 15 gms. to the square meter, are dipped in the bath thus prepared. These, after having been cleared of excess liquid and dried at about 50° C., are heated for 40 seconds at 125°–130° C. Sheets thus treated show a remarkable resistance to water.

EXAMPLE NO. 3

140 parts by weight of diureido-1,6 hexane and 270 parts by weight of a 37% aqueous solution of methanal, are mixed together and heated at about 80° C. until the diureido hexane is dissolved. The temperature is then allowed to go down to 60° C. and to this mixture are added 250 parts by weight of methanol containing 6.5 parts by weight of sodium hydroxide.

Then all is boiled under reflux.

The reaction is stopped before the product becomes resinified, by cooling and neutralizing with diluted chlorhydric acid. 50 to 60 minutes boiling, or more, is generally suitable.

The mixture thus obtained contains diureido-1,6 hexane N-methoxymethylated. If desired the water and excess alcohol present can be eliminated by distillation, preferably under reduced pressure.

Four parts by weight of this mixture as it remains after neutralization, are diluted in 100 parts by weight of water containing 30 volumes of ethanol.

This preparation is then brought to pH 5.5 with the help of phosphoric acid.

Sheets of filter paper, plunged in this bath and treated as indicated in the other examples, after having been heated to a temperature of between 120° and 130° C. for 60 to 80 seconds, show a notably increased resistance when brought into contact with water. The filtering power remains good and these filters can be used again several times.

Very thin sheets of sulfite paper, treated in the same manner, show notably better qualities and specially a notably increased resistance to water.

EXAMPLE NO. 4

232 parts by weight of diureido-1,5 (carbamyl-3 aza-3 tetracarbane), are dissolved by heating in 420 parts of a 37% aqueous methanal solution.

Immediately the temperature has gone down to 25° C., a solution of sodium hydroxide is added, to alkalinize and bring the pH to about pH 9. It is then heated for 60 minutes between 50° and 60° C. The temperature is then allowed to go down to 20° C. and it is neutralized with diluted chlorhydric acid.

The water present can be evaporated if desired, preferably by distilling under reduced pressure. In this case it is better that the solution has a pH of slightly more than 7, in order to avoid resinification of the product.

The operation is performed at a temperature below 40° C., nevertheless higher temperatures may be used.

The residue obtained after evaporation of the water consists chiefly of diuredo-1,5 (carbamyl-3 aza-3 tetracarbane) N-hydroxymethylated.

Three parts by weight of this residue are softened and dispersed in a little ethyl alcohol and thinned out in 100 parts of water.

Sulphuric acid is then added to this preparation to bring its pH to 5.

Different thicknesses and qualities of paper are treated in this bath. These, after being dried at 30° C. and heated at 120° C. for 120 to 180 seconds, show resistance to water. Kraft-bleached paper, after treatment, shows a remarkable resistance, even after 30 days immersion in water.

EXAMPLE NO. 5

108 parts by weight of diureido-1,7 heptane are mixed with 220 parts by weight of a 30% aqueous methanal solution. This neutralized mixture is heated at 80°–90° C. until the diureido-1,7 heptane is dissolved. Immediately the temperature has returned to 20° C., the pH is brought to 8.5 by means of caustic soda. It is then heated and maintained at a temperature of between 40° and 60° C. for about one hour, still leaving the pH within the indicated limit.

It is cooled and neutralized. The water present is distilled under reduced pressure at about 35°–40° C., until a dense residue is obtained, which contains about 85% dry residue. The greater part of this product is represented by the diureido-1,7 heptane N-hydroxymethylated.

Two parts by weight of this residue are dispersed in 100 parts of water and then 0.05 part by weight of adipic acid are added.

Sheets of paper, immersed in this preparation and compressed to remove all excess, are dried at about 45° C. and submitted for 60 to 120 seconds to a temperature of 125°–130° C. The results obtained are comparable to those of Example No. 1.

EXAMPLE NO. 6

Starting from diureido-1,4 butane and proceeding in the same manner as in Examples No. 1 and No. 2, a dry extract containing diureido-1,4 butane N-methoxymethylated is prepared. Two parts by weight of this extract are dissolved in 50 parts of ethanol and the mixture is brought to 100 total weight by adding water and 0.04 part ammonium chloride.

Sheets of paper immersed in this preparation after being dried at 40° C. and subsequently heated at 110°–120° C. show good water resistance.

EXAMPLE NO. 7

150 parts by weight of diureido-1,2 ethane are added to 330 parts by weight of a previously neutralized 37% aqueous solution of methanal. This mixture is then brought to about 70°–80° C., until the diuredio-1,2 ethane is dissolved. After this it is cooled down to 40°–45° C. and by means of a 5% solution of sodium hydroxide, its pH is brought within the range of pH 8 to pH 9.

The preparation is first maintained at 40°–50° C. for about 45–60 minutes then cooled to room temperature and neutralized. It contains the derivative, N-hydroxymethylated diureido-1,2 ethane, in the amount of 55% of its weight.

In this concentration and at room temperature, the preparation tends to thicken and jellify.

In any case, it liquifies easily at about 50° C. and is soluble in water.

40 parts of this concentrated solution of the derivative, N-hydroxymethylated diureido-1,2 ethane are then dissolved in 1000 parts of water and then 1.2 parts by weight of ammonium nitrate are added.

Sheets of "laid" quality cigarette paper, weighing 20 gms. to the square meter and containing about 30% of mineral filling of calcium carbonate basis, are immersed in this diluted solution, at room temperature. After having eliminated the excess of liquid from the surface of the paper, it is dried and then submitted for 60 seconds to a temperature of 125°–130° C.

Sheets thus treated burn normally without any abnormal odour.

In a wet condition they have a remarkable mechanical resistance, which remains good after two hours boiling in water.

EXAMPLE NO. 8

A sheet of paper of 25 gms. to the square meter dry weight, is sprayed, at the outlet of the paper ma-

chine, with an aqueous solution of the derivative, N-hydroxymethylated diureido-1,2 ethane, prepared as has been described in Example No. 7, to which is added phosphoric acid to bring its pH to 6, before entering the driers.

These are the normal steam heated cylinder type with a pressure of 2 kilos to the square centimeter.

The concentration and quantity of solution sprayed, are regulated in such a way as to depose on the paper a quantity of the derivative, N-hydroxymethylated diureido-1,2 ethane corresponding to the 3% of the dry weight of the paper.

The sheet of paper is then heated for 50 seconds at 120°–130° C. In a wet condition it presents a remarkable mechanical resistance, as the following tests show.

These tests are executed on a Mullen apparatus with wet paper samples which have been immersed respectively for 5, 15 and 20 minutes in distilled water at 20° C. and after elimination of excess water under a pressure of 2 kilos per square centimeter.

They give the following results:

Bursting resistance in kilos per square centimetre

Dry sample (not immersed)	0.66
Sample immersed for 5 minutes	0.67
Sample immersed for 10 minutes	0.60
Sample immersed for 120 minutes	0.61

Bursting Index

Dry sample (not immersed)	26.6
Sample immersed for 5 minutes	27.0
Sample immersed for 10 minutes	24.2
Sample immersed for 120 minutes	24.5

Percentage of resistance in wet condition to that of dry condition

Sample immersed for 5 minutes	101
Sample immersed for 10 minutes	90.9
Sample immersed for 120 minutes	92.4

Moreover, it is to be observed that the same quality paper, manufactured however without adding the derivative, N-hydroxymethylated diureido-1,2 ethane, presents practically no resistance immediately it is brought into contact with water.

It will be understood that the invention is susceptible to modification in order to adapt it to different usages and conditions, and, accordingly, it is desired to comprehend such modifications within the invention as may fall within the scope of the appended claims.

What is claimed is:

1. A process for changing and improving the properties, particularly the wet strength, of products obtained from cellulosic pulp comprising the steps of

(1) applying to the surface of a cellulosic paper capable of imbibing liquids N-hydroxymethylated 1,6-diureido-hexane in a liquid carrier;

(2) permitting the paper to imbibe the N-hydroxymethylated 1,6-diureido-hexane in a liquid carrier; in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

2. A process for changing and improving the properties, particularly the wet strength, of products obtained from cellulosic pulp and crude and refined paper pulps, comprising the steps of

(1) applying to the surface of a paper capable of imbibing liquids N-hydroxymethylated 1,5-diureido-carbanyl-3-aza-3-tetracarbane in a liquid carrier;

(2) permitting the paper to imbibe the N-hydroxymethylated 1,5-diureido-carbanyl-3-aza-3-tetracarbane in a liquid carrier; in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

3. A process for changing and improving the properties, particularly the wet strength, of products obtained from cellulosic pulp and crude and refined paper pulps, comprising the steps of

(1) applying to the surface of a cellulosic paper capable of imbibing liquids N-hydroxymethylated 1,7-diureido-heptane in a liquid carrier;

(2) permitting the paper to imbibe the N-hydroxymethylated 1,7-diureido-heptane in a liquid carrier; in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

4. A process for changing and improving the properties, particularly the wet strength of products obtained from cellulosic pulp in a liquid carrier comprising the steps of

(1) applying to the surface of a paper cellulosic capable of imbibing liquids N-hydroxymethylated 1,8-diureido-dicarbanyl-(3,6)-diaza-3,6-hexacarbane in a liquid carrier;

(2) permitting the paper to imbibe the N-hydroxymethylated 1,8-diureido-dicarbanyl-(3,6)-diaza-3,6-hexacarbane in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

5. A process for changing and improving the properties, particularly the wet strength of products obtained from cellulosic pulp comprising the steps of

(1) applying to the surface of a paper capable of imbibing liquids N-hydroxymethylated 1,2-diureido-ethane in a liquid carrier;

(2) permitting the paper to imbibe the N-hydroxymethylated 1,2-diureido-ethane in a liquid carrier; in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

6. A process for changing and improving the properties, particularly the wet strength of products obtained from cellulosic pulp, comprising the steps of

(1) applying to the surface of a cellulosic paper capable of imbibing liquids N-methoxymethylated 1,2-diureido-ethane in a liquid carrier;

(2) permitting the paper to imbibe the liquid in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80–130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without mate-

rially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

7. The method as described in claim 1, wherein said aqueous dispersion is applied by spraying.

8. The method as described in claim 1, wherein said aqueous dispersion is applied by immersing the paper therein.

9. The process described in claim 1 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

10. The process described in claim 2 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

11. The process described in claim 3 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

12. The process described in claim 4 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

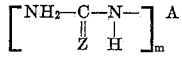
13. The process described in claim 5 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

14. The process described in claim 6 wherein the liquid carrier of step (1) is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

15. A process for changing and improving the properties, particularly the wet strength of products obtained from cellulosic pulp, comprising the steps of

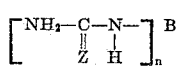
(1) applying to the surface of a cellulosic paper capable of imbibing liquids, a reaction product in a liquid carrier, said reaction product selected from the group consisting of N-hydroxymethylated, N-alkoxymethylated, and mixtures thereof of polyureas selected from the group consisting of

(*a*) saturated acyclic and alicyclic compounds of the general formula



wherein *m* is an integer from 2 to 4. A^m represent a hydrocarbon radical selected from the group consisting of unsubstituted and substituted saturated aliphatic chain radicals having from 2 to 16 carbon atoms and unsubstituted and substituted saturated alicyclic radicals of 6 carbon atoms and aromatic compound of from 6 to 7 carbon atoms.

(*b*) saturated hetero-acyclic compounds of the general formula



wherein *n* is an integer from 2 to 4 and B is an aliphatic chain radical of from 4 to 8 carbon atoms in which at least one atom selected from the group consisting N,O, and S, is interposed in the sequence of carbon atoms forming said chain, the nitrogen atom interposed in said sequence being bonded with two of its three valences in the chain and with its third valence to the radicals selected from the group consisting of hydrogen and

and Z in all atom formulas being an atom selected from the group of O or S.

(2) permitting the paper to imbibe the substance in amounts corresponding to an incorporation of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper;

(4) heating the paper to a temperature between 80 to 130° C. for about 40 to 180 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

16. The process described in claim 15 wherein the substance is incorporated in amounts corresponding to an incorporation of between 1% and 6% of the dry pulp weight of the paper.

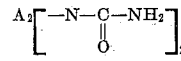
17. The process described in claim 15 wherein the liquid carrier is selected from the group consisting of water, lower saturated aliphatic alcohols, and mixtures thereof.

18. The process described in claim 15 wherein the polyurea is at least partially methoxymethylated.

19. The process described in claim 15 wherein the polyurea is at least partialy ethoxymethylated.

20. A process for changing and improving the properties, particularly the wet strength, products obtained from cellulosic pulp comprising the steps of

(1) applying to the surface of cellulosic paper capable of imbibing liquids in a dispersion medium selected from the group consisting of water, methanol, ethanol, and mixtures of water and ethanol; of a reaction product selected from the group consisting of N-hydroxymethylated, N-alkoxymethylated and mixtures thereof of polyureas having the general structural formula



wherein A is a structural radical selected from the group consisting of straight carbon chain radicals having from 2 to 7 carbon atoms and carbanyl-(3)-aza-(3)-tetracarbane;

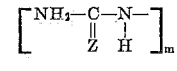
(2) permitting the paper to imbibe the liquid in amounts corresponding to an incorporation of said polyureas of between 0.25 and 12% of the dry pulp weight of the paper;

(3) removing the excess of liquid from the paper; and

(4) heating the paper to a temperature between 80 to 130° C. for about 40 to 240 seconds and longer; thereby increasing wet strength of the paper without materially changing its appearance, pliability, porosity, feel and its power of absorbing water and inks.

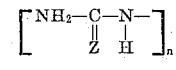
21. A celulosic paper containing, heat-condensed therein, amounts ranging from 0.25% to 12% of the dry pulp weight of the paper of a reaction product selected from the group consisting of N-hydroxymethylated, N-alkoxymethylated, and mixtures thereof of polyureas selected from the group consisting of

(*a*) saturated acyclic and alicyclic compounds of the general formula



wherein *m* is an integer from 2 to 4. A represent a hydrocarbon radical selected from the group consisting of unsubstituted and substituted saturated aliphatic chain radicals having from 2 to 16 carbon atoms and unsubstituted and substituted saturated alicyclic radicals of 6 carbon atoms and aromatic compound of from 6 to 7 carbon atoms.

(*b*) saturated hetero-acyclic compounds of the general formula



wherein *n* is an integer from 2 to 4 and B is an aliphatic chain radical of from 4 to 8 carbon atoms in which at least one atom selected from the group consisting N, O, and S, is interposed in the sequence of carbon atoms forming said chain, the nitrogen atom interposed in

said sequence being bonded with two of its three valences in the chain and with its third valence to the radicals selected from the group consisting of hydrogen and

and Z in all atom formulas being an atom selected from the group of O or S.

References Cited in the file of this patent

UNITED STATES PATENTS

2,380,133	Waltmann et al.	July 10, 1945
2,400,016	Meyer	May 7, 1946
2,624,686	Kamlet	Jan. 6, 1953
2,699,435	Auten et al.	Jan. 11, 1955
2,734,890	Bortnick	Feb. 14, 1956