

## UNITED STATES PATENT OFFICE

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## HIGH-WET-STRENGTH PAPER

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This invention relates to the art of paper making, and a principal object of the invention is to provide papers having a relatively high degree of wet-strength. This application is a continuation-in-part of my application Serial No. 91,963, filed July 22, 1936.

Another object of the invention is to provide paper whose wet-strength is materially increased without unduly modifying the normal desirable characteristics of the paper or such properties as water absorbency and softness required in certain classes of paper.

Another and more specific object of the invention is to provide soft, absorbent papers, such as those employed for towels and toilet tissues, that possess a relatively high degree of strength and resistance to surface disintegration while in the wet state.

In the normal paper making process cellulosic fibres, i. e., fibres derived from various plant materials and consisting essentially but not entirely of cellulose, are deposited from suspension in water to produce an interfelted web. A considerable amount of adhesion or bonding between the individual fibres in contact with each other develops upon drying this web, and it is this peculiar property of cellulose that accounts for the strength of normal papers.

It is thought that at the point of contact between two fibres in a dry sheet of paper there is a minute portion of the cellulose structure which may be considered to be held by the two fibres in common. In the normal paper this cellulose structure is hydrophilic, not in the sense of any of the material actually being soluble in water but in the sense of being capable of associating itself intimately with water and thus having its cohesive strength substantially reduced, so that the bonding, cementation, or adhesion between the cellulose fibres of conventional papers has had the disadvantage of losing its strength when wetted with water. Thus, most papers when wet have only a relatively small per cent., say 5 to 10%, of the strength that they possess when dry.

The present invention provides a means for modifying the cellulose structure constituting the bonding or cementation between the individual fibres so that it shall remain strong when the paper is wetted.

In carrying out the invention, the dry or partially dry web of paper is impregnated with a water solution containing a substance or substances capable under the proper heat and catalytic conditions of polymerizing to a water-

insoluble condition. In order that the wet-strengthening agent may actually penetrate the cellulosic structure of the individual fibres, it is important that it exist initially as a true solution in water. After the penetration into the fibres the agent must be capable of polymerizing rapidly to the insoluble state under relatively mild conditions of heat, e. g., under the conditions of normal drying of paper on a paper machine or paper treating machine. Materials fulfilling the above requirements are found among the substances capable of forming synthetic resins.

In proceeding in accordance with the invention, therefore, there are introduced into the cellulose structure resin-producing ingredients either in the unreacted, the unpolymerized, or the partially reacted state, and thereafter the reaction or a completion of the reaction between these ingredients is effected to produce the desired result. The materials from which the final resin is formed should enter the cellulose structure in the form of a water solution, and for this condition to be fulfilled, the materials should be in the form of compounds of relatively low molecular weight and soluble in water. These materials having penetrated the cellulose structure are caused to undergo a condensation or polymerization, or both, as a result of the application of heat in the presence of a catalyst, and this reaction results in the formation within the cellulose structure of a water insoluble resin, the presence of which, particularly in that part of the cellulose structure where two fibres have been dried in contact with each other, has the result of rendering the cellulose bond substantially unaffected by water. Where the properties of absorbency and softness are required, it is essential that no large proportion of the resin shall exist between the fibres of the paper outside of the cellulose bonding structure, since excess resin has the effect of increasing the stiffness of the sheet.

Several materials may be used in this process, such, for example, as urea and formaldehyde, urea and hexamethylenetetramine, thiourea and formaldehyde, urea and acetaldehyde, and urea and butyraldehyde, the said aldehydes being saturated aliphatic aldehydes having from 1 to 4 carbon atoms. In addition, numerous other materials are potentially capable of affording the desired results, such, for example, as urea and furfural, phenol and formaldehyde, phenol and furfural, phenol and butyraldehyde, phenol and acetaldehyde, phenol and hexamethylenetetramine, and phthalic anhydride and glycerol. In general, the materials which are potential agents

for accomplishing the purpose of this invention may be defined in the following terms:

1. They should be soluble in water;
2. They should exist in the cellulose impregnation stage in the form of sufficiently small molecules to permit their ready penetration into the cellulose structure; and
3. They should be capable after penetration into the cellulosic structure of undergoing a reaction resulting in the formation of a water insoluble, resin-like material.

I am aware that the impregnation of cellulosic materials with solutions more or less similar to the above has been the subject of previous inventions. For example, urea and formaldehyde has been suggested for rendering regenerated cellulose (rayon) fabrics resistant to creasing. These processes, however, involve the use of such quantities of urea-formaldehyde that when applied to paper of the sort contemplated by this invention they destroy the essential physical properties of the paper. Further, a study of the effect of urea-formaldehyde on rayon fabrics would not suggest the very different function disclosed by this invention. Also, it has been suggested to use urea-formaldehyde to prevent the "swelling" of cellulosic materials. Here again the application of the previous invention in such a manner as to substantially reduce swelling destroys certain physical properties of paper which it is the purpose of this invention to preserve. Further, the use of urea-formaldehyde as specified in this invention has no appreciable effect on the swelling characteristics of the material.

It is an essential feature of this invention that the polymerization or insolubilizing reaction take place quickly and easily in order to permit the incorporation of the process as a step in the manufacture of paper. In order to realize this the polymerization reaction must be accelerated by the use of a catalyst. With urea-formaldehyde, phenol-formaldehyde, and thiourea-formaldehyde the most suitable catalyst is an acid or acid salt. I may, for example, use a mineral acid such as sulphuric acid, hydrochloric acid, or phosphoric acid, or I may use an organic acid such as acetic acid or formic acid, or I may use an acid salt such as ammonium chloride, sodium bisulphate, aluminum sulphate, or zinc chloride; or I may use a neutral salt which becomes acid under the heat conditions incidental to drying the impregnated sheet, for example, secondary ammonium phosphate, or ammonium sulphite.

With the use of urea-formaldehyde, for example, it is not difficult to select a catalyst which will induce a rapid polymerization under the heat conditions incidental to the drying of paper since any material capable of producing a mild acid condition will serve. It is, however, more difficult to select a catalyst which will give a relatively stable stock solution when mixed with urea-formaldehyde, and which need not be removed from the finished sheet. Secondary ammonium phosphate has been found to fulfill these conditions most satisfactorily.

Of the various combinations of materials mentioned above, urea and formaldehyde are particularly well suited for the practice of the invention in that, in an intermediate or partially reacted stage these materials are productive of a water-soluble solid. Depending upon the proportions of formaldehyde and urea, this water-soluble solid takes the form either of monomethylolurea or dimethylolurea, or a mixture of

the two. Dimethylolurea has been found best suited to the requirements of the present invention, although it is sometimes desirable to employ a mixture of the two ureas.

Dimethylolurea is available in the trade, and its use insures an introduction of the materials in exact proportions and materially facilitates the process as a whole. Further advantages in the use of dimethylolurea reside in the rapidity with which polymerization takes place and in the mild temperature and catalytic conditions necessary; in the absence of any tendency of the polymerized resin to decrease the absorbency of the paper; in the stability of the dimethylolurea solution; in cheapness of raw materials; in the fact that no residual color or odor is left in the treated paper; and in the further fact that there is no decomposition of the resin with age.

In a specific procedure by way of example, paper is impregnated to saturation by any suitable means with a water solution of the following composition:

|                      | Per cent by weight |
|----------------------|--------------------|
| Dimethylolurea ..... | 1.0                |
| Sulphuric acid ..... | 0.05               |

The paper is then dried, preferably at a relatively low temperature, say below 150° F., in order to insure against polymerization while the paper is in the wet or moist state, or until the water phase is reduced to that amount which is contained within the fibres. A considerable degree of wet strength will result regardless of the method of drying, but the maximum of wet strength may only be obtained by initial low temperature evaporation. Subsequent to drying, the paper web is heated to a temperature sufficient to convert the water-soluble compound into a substantially water-insoluble urea-formaldehyde resin, which resin is in a substantially cured condition. The extent of this heating subsequent to drying is not great. It has been found that the amount of heating received by a sheet of paper passing through the drier section of a paper machine in the normal papermaking process is sufficient to cause adequate polymerization.

It is apparent that substantially the same results may be obtained by employing a mixture of urea and formaldehyde rather than dimethylolurea, and in the case of some of the other resin-producing materials, it is necessary to keep the initial solution merely as a mixture in order to retain water solubility. A suitable catalyst may be incorporated in the mixtures in their unreacted state and substantially the same procedure followed as has been described above as to drying the treated sheet and subsequently raising the temperature of the sheet to a point effecting the resin-producing reaction. In such cases, it is desirable to employ the materials in amounts and proportions, readily determinable by those familiar with the art, to afford the desired result without leaving any excess of the materials in the paper sheet, either in the form of the completed resin or in their initial individual forms. The relative proportions of the urea and formaldehyde may be stated, for example, as approximately 1 to 1; and if the materials are added to the paper in amount of about 2% of the weight of the latter, the substantial increase in wet-strength is obtained without appreciable modification in other respects of the normal paper characteristics. It will be apparent that the physical properties of

the finished sheet may be varied by using more or less of the resin-forming ingredients.

If dimethylolurea is used it may be prepared by any of the well known methods, but it has been found that the maximum wet-strength is obtained by using the following procedure; urea is dissolved in 37% formaldehyde solution (commercial formalin) in the proportion of 5 parts by weight of urea to 4 parts by weight of HCHO or approximately two mols of HCHO to one mol of urea. Other proportions will produce wet-strength, but it has been found that a higher proportion of urea decreases the amount of wet-strength obtained and a greater proportion of formaldehyde increases the cost and gives residual formaldehyde which must be disposed of. Enough sodium carbonate or other alkali is added to the above solution to give a definitely alkaline reaction. About 0.05%  $\text{Na}_2\text{CO}_3$  on the basis of urea+formaldehyde is a convenient amount. The solution is allowed to stand from 4 to 12 hours and is then diluted to a suitable concentration with water. After addition of the catalyst, this solution is ready for use in the wet-strength process. The solution so prepared is found superior to a mixture of uncombined urea and formaldehyde and to dimethylolurea prepared by heating.

The acid catalysts which may be employed are such as those already listed above and the amount of these catalysts required is quite small. For example, using sulphuric acid, 0.05% acid in the impregnating solution gives the maximum wet-strength. More than 0.1% sulphuric acid has a destructive action on the fibre. In using aluminium sulphate approximately 0.1% gives the best results, and closely similar amounts are required for the other salts.

It is undesirable to leave unneutralized acidic catalyst in the finished paper, and the paper may, therefore, be treated after the application of the wet-strength process with a suitable alkaline solution. A solution of this character may consist of a mild alkali such as sodium bicarbonate, di-sodium phosphate, sodium borate, or similar salts, in such strength as to neutralize the catalyst and at the same time leave the paper essentially neutral. A solution of 0.3% sodium bicarbonate applied in an amount of 20% of the weight of the dry paper is an effective neutralizer. The paper is again dried after this treatment and the resulting sheet constitutes the finished product.

It is to be remembered that the conversion of dimethylolurea to the insoluble resin takes place slowly in acid solution even at room temperature. For this reason a solution containing any of the above catalysts must be used immediately after the addition of the catalyst, and must be used as a relatively dilute solution. Further, the handling of acidic aqueous solutions presents serious engineering difficulties such as corrosion of machinery and equipment of all sorts. For these and other reasons it has been found more convenient to use as catalysts certain salts which in the initial state are neutral or slightly alkaline but which, upon exposure to the heat incident to drying the impregnated paper, develop a mild acid condition which causes the polymerization to take place. Examples of such salts are tri-ammonium phosphate,  $(\text{NH}_4)_3\text{PO}_4$ , secondary ammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , and ammonium sulphite,  $(\text{NH}_4)_2\text{SO}_3$ . The first two salts are converted by heat into the acidic mono-ammonium phosphate, while the third is con-

verted to ammonium sulphate. The use of these catalysts has been found to be very convenient in practice. The claims reciting the presence in the paper of "an acid-polymerized resin" include resins polymerized under acid conditions derived either by reason of the presence of an acid or acidic substance at the time of polymerization; thus, the claims include the use of catalysts which may be neutral or slightly alkaline but which upon exposure to heat develop a mild acidic condition which causes polymerization.

As a further practical example of the way in which the invention may be carried into effect employing a catalyst of this type, a sheet of dry paper, for example paper toweling, is sprayed by any convenient means with a solution consisting of the following materials:

|                                   | Per cent |
|-----------------------------------|----------|
| Dimethylolurea .....              | 3.0      |
| Secondary ammonium phosphate..... | 0.25     |
| Remainder, water.                 |          |

The moisture content of the sheet immediately after spraying should be about 25-30%. This would mean the application of about 1.0% urea-formaldehyde resin on the basis of the paper. The paper is then dried on steam-heated rotating cylindrical driers as normally used in the paper industry. It has been found that a drier temperature of 275° to 300° F. and a total time of contact between the paper and the driers of about 30 seconds gives very good results. Paper so treated would normally have a wet-strength of 35-50% of the dry-strength or 4-6 times that of the untreated paper. The dry-strength would be increased only slightly, say 10 to 15%.

As another example partially dried paper may be sprayed on a papermaking machine. Suppose for example the paper at the point of spraying contains 40% water. Then the spraying solution would consist of the following:

|                                   | Per cent |
|-----------------------------------|----------|
| Dimethylolurea .....              | 20       |
| Secondary ammonium phosphate..... | 1.5      |

The amount of this solution applied would be 6% of the weight of the dry paper, and the moisture content of the sheet would be increased from 40% to 42%. The paper is then dried in the normal way. With the use of the ammonium phosphate catalyst no neutralization step is required.

The degree of wet-strength obtained, other things being the same, is within certain limits a function of the amount of urea-formaldehyde used in proportion to the fibre treated. For example, with paper toweling the use of urea-formaldehyde in amount of 1% on the basis of fibre increases the wet-strength approximately four to five times. The use of 2% increases the wet-strength approximately six to seven times. In either case, the dry strength and other physical properties of the paper are substantially unchanged. The fact that there is substantially no change in the dry-strength of the paper is to be particularly noted, since this indicates that very little, if any, of the resin is acting as an additional interfibre cementing medium. This is accounted for by the fact that the urea-formaldehyde resin, when used under the conditions specified and in the proportions contemplated by the invention, is sufficiently soluble to remain in solution until the liquid phase has been reduced by drying to that amount which is held essentially within the fibres themselves.

Quantities of urea-formaldehyde less than .5%

of the fibre have very little effect on the wet-strength, while quantities greater than 3% have an appreciable hardening or stiffening effect. I have found in effect that the use of up to approximately 3% of resin results in an inconsiderable increase in the stiffness of the paper, whereas the wet-strength of the paper increases rapidly, as indicated above. Beyond 3% of resin and up to approximately 5%, the increased stiffness while appreciable is still inconsiderable as compared with the great increase in wet-strength. Beyond approximately 5% of resin, however, the rate of increase of wet-strength falls off so rapidly that the advantage gained in this respect is not sufficient, where the quality of softness in the product is required, to offset the disadvantage of the increasing hardness.

It is to be noted that fibres treated as above described are never water-repellent. If the resin is used in such large amounts, say in excess of 5% on basis of fibre weight, that considerable amount of condensation product exists between the fibres, absorbency or penetration of water into the interfibre spaces is impaired, but no apparent water-repellency, as such, exists.

In the application of the present invention certain modifying ingredients may be used along with the urea-formaldehyde. In particular, the use of protein matter, e. g., soya bean protein, casein or gelatin in amounts of 10% to 50% of the urea-formaldehyde has the effect of making the paper more resistant to exposure to water over long periods of time and at elevated temperatures. In the foregoing description, the preparation of a resin formed by reacting a urea and an aldehyde is described, and the use of a catalyst in the preparation of the resin from the urea and the aldehyde is recommended. In the claims, the phrase "a resin formed by the reaction of a urea and an aldehyde only" is employed to distinguish the urea-aldehyde resin from a product in which a third material is one of the resin-forming ingredients with the urea and the aldehyde in the preparation of the resin. This expression in the claims, of course, includes the preparation of the resin from a urea and an aldehyde in the presence of a catalyst.

In previous proposals paper has been heavily filled with resins to an extent largely modifying the normal paper characteristics, but the distinctions between these prior products and the processes by which they are produced and those according to the present invention will be apparent from the foregoing description.

I claim:

1. A high-wet-strength paper containing from approximately .5 of 1% to 5% on the basis of the dry weight of the paper, of a resin formed by reacting a urea and an aldehyde only, said aldehyde being a saturated aliphatic aldehyde

having from 1 to 4 carbon atoms and said resin being in substantially cured condition.

2. A high-wet-strength paper containing from approximately .5 of 1% to 3% on the basis of the dry weight of the paper, of a resin formed by reacting a urea and an aldehyde only, said aldehyde being a saturated aliphatic aldehyde having from 1 to 4 carbon atoms and said resin being in substantially cured condition, said resin-containing paper having a marked increase in wet-strength and substantially the water-absorbency and softness of the same paper free of resin.

3. A high-wet-strength paper containing approximately 2% on the basis of the dry weight of the paper, of a resin formed by reacting a urea and an aldehyde only, said aldehyde being a saturated aliphatic aldehyde having from 1 to 4 carbon atoms and said resin being in substantially cured condition.

4. A high-wet-strength paper containing from approximately .5 of 1% to 5%, on the basis of the dry weight of the paper, of an acid-polymerized resin formed by reacting a urea and an aldehyde only, said aldehyde being a saturated aliphatic aldehyde having from 1 to 4 carbon atoms and said resin being in substantially cured condition.

5. A high-wet-strength paper containing from approximately .5 of 1% to 3%, on the basis of the dry weight of the paper, of an acid-polymerized resin formed by reacting a urea and an aldehyde only, said aldehyde being a saturated aliphatic aldehyde having from 1 to 4 carbon atoms and said resin being in substantially cured condition, said resin-containing paper having a marked increase in wet-strength and substantially the water-absorbency and softness of the same paper free of resin.

6. A high-wet-strength paper containing from approximately .5 of 1% to 5% on the basis of the dry weight of the paper, of a resin formed by reacting urea and formaldehyde only, said resin being in substantially cured condition.

7. A high-wet-strength paper containing from approximately .5 of 1% to 3%, on the basis of the dry weight of the paper, of an acid-polymerized resin formed by reacting urea and formaldehyde only, said resin being in substantially cured condition, said resin-containing paper having a marked increase in wet-strength and substantially the water-absorbency and softness of the same paper free of resin.

8. A high-wet-strength paper containing from approximately .5 of 1% to 5% on the basis of the dry weight of the paper, of an acid-polymerized resin formed by reacting a urea and formaldehyde only, said resin being in substantially cured condition.

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