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METHOD OF ENHANCING THE WET STRENGTH OF PAPERS

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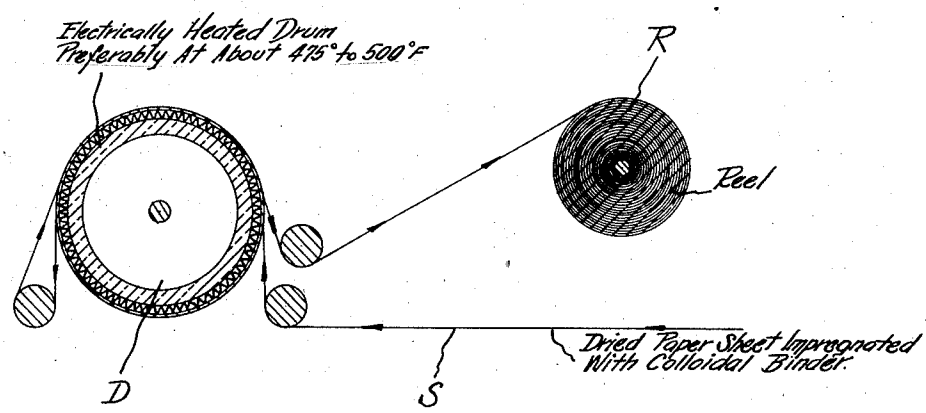

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METHOD OF ENHANCING THE WET-STRENGTH OF PAPERS

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This invention relates to a method of enhancing the wet-strength of various kinds of papers, including substantially waterleaf papers and papers impregnated with colloidal binders of the nature of glue, casein, viscose, etc., which are introduced into the paper as aqueous solutions or suspensions and which, upon drying of the paper, are more or less irreversibly set to impart water-resistivity or high wet-strength to the paper.

I have discovered that the water-resistivity or wet-strength of substantially waterleaf papers and papers impregnated with binders of the foregoing character may be enhanced to an amazing degree by the application of heat to the dry paper, and advantageously by the momentary application of intense heat to the paper, that is, heat of such intensity as would injure the paper if applied for more than a certain short period of time. Such intense but momentary heating of the substantially waterleaf or binder-impregnated paper may, pursuant to the present invention, be advantageously performed after the paper has been dried as usual, for instance, on steam-heated drier drums at temperatures of about 212° to 265° F. While various temperatures of heating upwards of about 300° F. may be employed according to my process in the heat-treatment of the predried, substantially waterleaf or binder-impregnated paper for the purpose of enhancing greatly its water-resistivity or wet-strength, I have found it in many instances preferable to work within a temperature range of about 400° to 650° F., for instance, to expose the dry paper to a temperature of about 475° to 500° F., as at such temperature it is possible to develop practically instantly a phenomenal increase in the wet-strength of the paper without injuring it and to do so inexpensively with a comparatively small heating surface while the paper is traveling continuously and at high speed, for instance, from the dry end of a papermaking or impregnating machine.

I shall now give instances of the application of my invention to demonstrate the remarkable and advantageous results that can be realized thereby. In one case, my aim was to produce a paper of maximum wet-strength such as is of value in wrapping wet vegetables, such as lettuce and celery, or lining the crates in which such vegetables in iced condition are packed and shipped. To this end, I may impregnate a waterleaf paper sheet of any suitable basis weight and fiber composition with a glue solution containing about 3% glue, based on solution, and about 2% formaldehyde, based on glue. The sheet may be squeezed upon emergence from an impregnating bath of such glue solution, as by squeeze rolls, so that it retains about its own weight of the impregnating solution, whereupon it may be air-dried, say, at 70° to 100° F. When a sheet of kraft pulp paper of 47 pounds basis weight was thus impregnated and dried as usual, it was found to have a bursting strength (Mullen) of 12 pounds per square inch after a thorough soaking through with water effected by its submergence in a water bath for one-half hour. When an impregnated and dried sheet of similar character was, according to the instant invention, exposed for roughly one second to a temperature of about 475° to 500° F., its wet-strength, that is, bursting strength after similar water-submergence, was 35 pounds per square inch. This remarkable increase in the wet-strength of the paper sheet by momentary intense heating was had with practically no burning or other sensible injury thereof. The heating of the paper sheet for two seconds at such temperature increased its wet-strength to 39 pounds per square inch without significant burning of the fiber, but heating for a longer period did not enhance the wet strength of the paper materially and the paper became noticeably embrittled. When the paper was exposed to a temperature of 435° F., it was found possible to increase its wet-strength markedly by extending the time of its exposure to such temperature to about 40 seconds. An improvement may also be realized by exposing the paper to a temperature of 350° F. for about 1½ to 2 minutes.

As already indicated, it is preferable in many cases to expose the paper to maximum safe elevated temperature for a very short time. In this connection, it is to be borne in mind that heating of a rapidly moving paper sheet, for instance, a sheet traveling continuously at 200 to 400 feet per minute from the dry end of a paper-making or impregnating machine, requires extensive heating surface and that the provision of such heating surface and its maintenance at temperatures upwards of 300° F. is prohibitively costly. A one-minute heat treatment performed on a sheet traveling at a speed of 200 to 400 feet per minute obviously requires a heating surface 200 to 400 feet long, whereas, on the other hand, a one-second heat treatment reduces the length of the heating surface to 1/60th, that is, to only 3.3 to 6.7 feet. It is thus understandable why I prefer, especially in the case of high speed paper production, to conduct the heat treatment at about 475° to 500° F., which represent a temperature to which most papers can be exposed momentarily

without being materially injured, and to correlate such temperature with an area of heating surface and a paper speed corresponding roughly to about a one-second heating period. In some instances, I may go to an elevated temperature as low as 400° F. or to an elevated temperature as high as 650° F., depending upon such factors as composition of paper, surface texture, basis weight, etc.

Another example involving the use of my invention was centered about the production of paper toweling possessed of good absorbency as well as high wet-strength. In such case, an absorbent, waterleaf paper sheet of kraft pulp having a basis weight of 37 pounds was impregnated with a 2% aqueous solution of ammoniated casein, squeezed to a content of impregnating solution about equal to the dry weight of paper, and dried on the usual steam-heated drums at 240° F. The wet-tensile-strength of a one-half inch width strip of the resulting paper sheet averaged 1.5 pounds. In testing for wet-tensile-strength, strips one-half inch in width were pulled apart a few seconds after having been streaked transversely with a camel-hair brush wet with water. Since the dried impregnated sheet is quite water-absorbent, the test strips become wet through by the time the tensile load is applied thereto. A test similarly performed on the paper sheet before it was impregnated with a casein solution gave a wet-tensile-strength of 0.7 pound. When the dried, impregnated sheet was heated for one second at 475° to 500° F. and for about two to three minutes at 350° F., its wet-tensile-strength was increased to 2.5 pounds. The presence of a small amount of formaldehyde in the impregnating bath may boost the wet-strength values both before and after the "shot" of intense heat.

As already indicated, the short, high temperature heat-treatment of my invention may be advantageously applied to various binder-impregnated papers whose binder depends upon dehydration to render it relatively strong when rewet. Thus, papers impregnated with viscose solutions or suspensions and other aqueous binders, besides albuminous binders, appearing as wet-strengthening agents in paper may be made to exert a much greater wet-strengthening effect on the paper by such heat treatment even after the paper containing such binder has already been dried thoroughly, as ordinarily. Of course, the surprising enhancement in wet-strength of the paper to be gained by my invention varies with the different binders. The presence of formaldehyde or other tanning agent in solutions of glue, casein, or other albuminous binders, such as I may employ herein, which causes a tanning reaction on the binder during the momentary intense heating of the binder-impregnated paper, may be advantageous in that such reaction may sometimes be brought more nearly to completion and the finished paper product ordinarily has higher wet-strength than is otherwise the case.

It is to be understood that my invention may be advantageously applied no matter at what stage of paper-making the binder is infused into the paper sheet. Thus, in some instances, the glue, casein, viscose, etc., may be introduced into the bulk pulp or fiber preparatory to its sheeting on the paper making machine; or such binders may be applied, as by spraying, to the wet or freshly formed paper web before it reaches the dry end of the papermaking machine, for instance, in advance of the last press rolls. In the examples hereinbefore given, the substantially dry, absorbent waterleaf paper sheet as it issues progressively from the dry end of the paper-making machine may be passed progressively through a bath of the binder solution, excess solution removed from the sheet immediately upon its emergence from the bath, as by squeeze rolls or scraper blades, whereupon the sheet may be redried to completion and finally exposed to a temperature upwards of about 300° F. for less than about two minutes, as hereinbefore described.

On the accompanying drawing, I have illustrated diagrammatically and conventionally one mode of heating the substantially dry, impregnated paper sheet as it is coming continuously from the dry end of a papermaking or impregnating machine. The paper sheet S, which may be traveling at a speed of about 200 to 400 feet per minute, may, as shown, be passed over an electrically heated steel shell or drum D, then be drawn back over itself to blanket the underlying paper, and finally be wound up as a roll R. The temperature of the drum, the extent to which the drum is wrapped by the paper sheet, and the speed of the sheet may be controlled to yield the best results according to the nature of the binder, the wet-strength desired in the finished paper product, and other circumstances of manufacture. The cost of such a heating instrumentality is relatively low, for it is of compact simple construction and easily operated and controlled. In some instances, it may be desirable to cool the paper before it is reeled or accumulated or to moisten it with a small amount of water, say, with about 5% to 7% of its own weight of water, but these expedients, being simply additive to the invention hereof and being readily accomplished in simple ways by those skilled in the art, need not be discussed in detail or illustrated.

While the invention hereof has been described as being applied to paper, it should be obvious that its utility may extend also to binder-impregnated woven fabrics and to carded or felted fiber webs, for instance, to carded cotton fiber webs or to wool felts wherein it may be desired to attain the highest wet-strengths by the use of binder-impregnants of the class hereinbefore described. I shall use in the appended claims the expression "interfelted fibrous sheet material" as covering carded webs, felts, and papers, as all such fibrous sheet material is characterized by a more or less interfelted fibrous structure or texture. So far as concerns the aspect of producing by my invention papers of the highest wet-strength, it will, of course be appreciated that the resulting papers might be of such high binder content as to be sized or water-repellent or, in the case of viscose or albuminous binders, such as glue and casein, be of such controlled binder content as to be water-absorbing and hence adapted for such uses as toweling, handkerchiefs, diaper linings, etc. It is obvious that the paper might be composed of various fibers or fiber mixtures, for instance, of the usual chemical wood pulps, such as sulphite or kraft, wood pulps refined to distinctly higher alpha cellulose contents, say, upwards of 93%, rag pulp, etc.; and the paper base might be formed with various degrees of absorbency, depending upon the use to which the final paper product is to be put. Indeed, the paper might contain non-cellulosic fibers such as wool and asbestos. Should my invention be applied to papers comprising esssentially only mineral fibers, such as asbestos, it becomes possible to heat the binder-impregnated paper at temperatures higher than 650° F. and for a time longer

than mere seconds by reason of the incombustibility of such fiber. In such latter case, the limit in temperature and time of final heat treatment is essentially that at which the binder is injured or decomposed by heat.

It is possible by applying the inventive principles hereof to produce impregnated paper products of surprisingly high dry tear or shear resistance coupled with unusually high wet-strength (Mullen and tensile). Thus, I may start with refined wood pulp ("Duracel") prepared by exposing kraft pulp to the refining action of comparatively strong alkaline liquor, for instance, so-called white liquor, at about room or slightly elevated temperature until the pulp has acquired an alpha cellulose content of about 90 to 92%. Such refined pulp in either unbleached or bleached condition is put into substantially uniform aqueous suspension preparatory to the papermaking operation while preserving its fiber length as much as is compatible with the realization of the desired substantially uniformly textured waterleaf paper sheet therefrom. The highly absorptive waterleaf paper sheet thus formed from such pulp is impregnated with a glue solution containing about 3% to 4% glue solids and a small amount of formaldehyde, squeezed to a glue content of about 3%, based on the dry weight of paper, air-dried at about room temperature, and finally brought into momentary contact with an intensely heated surface, as hereinbefore described. The resulting paper product is characterized by its unique combination of remarkably high wet-strength and very high dry tear-resistance. It might be noted that such a paper product is not only similar to vegetable parchment in its high wet-strength and wet scuff-resistance but far surpasses ordinary vegetable parchment in its toughness or dry tear-resistance. Because of the comparatively low glue content of such a paper product, it retains to a very large degree the flexibility of its waterleaf paper base as opposed to the comparatively stiff or brittle paper product produced when a similar paper base is impregnated to much higher glue content with a view toward giving it the high wet-strength of the paper product hereof simply by the usual passage over steam-heated drier drums of the papermaking or impregnating machine. The high dry tear-resistance of the paper product hereof is a reflection of the preservation of high average fiber length and fiber flexibility in the pulp entering into its waterleaf paper base; and the glue impregnant brought to the desired high degree of irreversibility by the intense heat treatment hereof is relied upon herein for the purpose of binding together the fibers and developing in the paper the wet-strength ordinarily sought to be gained by parchmentizing the fibers and thus sacrificing very significantly the tear-resistance in the paper product.

The invention hereof may be applied advantageously to waterleaf papers, that is, papers whose fabrication is carried out without the addition of binder to the paper-making stock at any stage of papermaking. Thus, by subjecting various substantially waterleaf papers to the "hot-shot" treatment hereof, it is possible to increase their wet-strength (Mullen, tensile, scuff-resistance, etc.) so markedly that the resulting papers have a Mullen wet-strength of more than about 8% of the dry Mullen strength, or a wet-tensile-strength of more than about 12% of the dry tensile strength. By the use of the expression "substantially waterleaf paper" in the specification and appended claims, I mean a paper fabricated in the complete absence of binder or sizing ingredient or containing binder or sizing ingredient of such type or in such small amount that when made as heretofore its wet-strength is markedly lower than the percentage ratios just expressed; and I do not mean to include by such quoted expression papers which have received a special chemical hydrating treatment, such as parchmentization. The "hot-shot" treatment may in the case of such substantially waterleaf paper involve subjecting such paper, after it has been dried in the usual way, to a one-second heating on each face by progressively passing the paper sheet as it is coming from the papermaking machine in contact with a surface heated to about 450° to 500° F. In this way, the wet-strength (tensile-strength of a strip ½" wide) of a waterleaf sheet of kraft toweling was increased from an initial value of 0.6# to 1.0#; of a waterleaf sheet composed of 50% kraft and 50% groundwood from an initial value of 0.6# to 1.2#; of a waterleaf sheet composed of refined wood pulp and intended for nitrating purpose from an initial value of 0.3# to 1.0#. Results of a similar order were obtained with various other papers, for instance, papers made from "Duracel" pulp, sulphite pulp, and cooked manila pulp. I shall now give in tabular form various characteristics of particular kinds of paper before and after a "hot-shot" treatment as above described.

**Tests before hot-shot*

Waterleaf papers	Mullen (points)		Tensile (#/½")		Tear	
	Dry	Wet	Dry	Wet	Dry	Wet
45# Kraft (100% "Ostrand")	48	1.3	13.6	1.1	102	26
48# "Duracel"	52	1.7	12.7	1.0	157	42
40# "Alpha N"	13	1.0	5.1	0.3	73	12

Tests after hot-shot

Waterleaf papers	Mullen (points)		Tensile (#/½")		Tear	
	Dry	Wet	Dry	Wet	Dry	Wet
45# Kraft (100% "Ostrand")	48	5.0	13.6	2.2	98	58
48# "Duracel"	52	5.4	14.4	2.1	128	82
40# "Alpha N"	14	1.3	4.9	0.9	67	24

* All test specimens of paper were soaked in water for one-half hour before the various wet tests were applied thereto; and the wet Mullen test was determined by bursting through 4 plies of the material under examination and dividing the gage reading by 4.

In other examples involving the application of the invention hereof, small quantities of binder, including casein and rosin size, were added to the papermaking stock after the manner of making the usual so-called engine-sized papers. Thus, ¼% casein, based on the dry weight of fiber, was precipitated from an ammonia-casein solution by means of alum in a papermaking stock of 50% kraft and 50% groundwood. The stock was converted on a papermaking machine into a sheet of creped toweling of 37# basis weight. When dried in the usual way, the paper toweling had a wet-tensile-strength of 0.6#, but when subjected after drying to contact on each of its faces for one second with a surface at about 450° to 500° F., the wet-strength of the paper toweling was increased to 2.5#. The resulting paper toweling was very absorbent and was not embrittled to any serious extent by the momentary heating. A similar improvement in the quality

of toweling stock of similar composition was had with the "hot-shot" treatment hereof conducted for 0.6 second with the heating surface at 600° F. and with the paper brought into contact with such surface only on a single face. Similar results were also had by subjecting engine-sized papers containing about 1.5% rosin to similar hot-shot treatments.

Other applications of the invention hereof were made to so-called tub-sized papers with similar advantageous results. The following tables give the characteristics of a certain grade of kraft paper both in waterleaf and tub-sized condition before and after the hot-shot treatment above described.

Tests before hot-shot

	Mullen (points)		Tensile (#/½")		Tear		Wet scuff rating
	Dry	Wet	Dry	Wet	Dry	Wet	
40# "Romal" kraft	37	4.0	10.0	1.3	96	70	8
Same paper tub-sized with sodium caseinate with deposition of 1% casein (based on weight of paper)	39	5.0	11.5	1.6	76	92	8

Tests after hot-shot

	Mullen (points)		Tensile (#/½")		Tear		Wet scuff rating
	Dry	Wet	Dry	Wet	Dry	Wet	
40# "Romal" kraft	36	14.3	10.4	3.3	62	99	30
Same paper tub-sized with sodium caseinate with deposition of 1% casein (based on weight of paper)	37	14.3	12.6	4.0	68	96	45

From the foregoing tables, it is apparent that the present invention makes possible in a simple and inexpensive way a marked and important increase in the utility of ordinary papers. Apropos of such increased utility, it might be noted that ordinary wrapping paper, for instance, is enhanced by the invention hereof tremendously in its resistance to breakage or scuff when thoroughly soaked with water and is hence rendered much more suitable as a wrapping paper which may be soaked, as by exposure to rain, or for fabrication into bags intended to hold moist or wet vegetables, or for use as a crate-liner, etc. The present invention thus makes possible among other things the production of paper products adapted to supersede in various fields of use requiring papers of high wet-strength such comparatively expensive prior art paper products as parchment papers, wax papers, etc.

So far as I know, I am the first to recognize that waterleaf papers and ordinary sized papers, for instance, rosin-sized wrapping paper, may be converted by the high temperature heating treatment hereof into finished paper products whose resistance to the disintegrating effect of water is enormously greater than that of the original papers. The finished waterleaf paper products hereof have, as already indicated, a Mullen wet-strength of more than about 8% of the dry Mullen strength and a wet tensile strength of more than about 12% of the dry tensile strength. The papers sized with rosin and heat-treated as hereinbefore described have a wet Mullen strength or wet tensile strength higher than about 25% of the corresponding dry tests; and such high wet-strength is inherent in the heat-treated paper base itself for the sizing agent in the heat-treated paper product having such high wet-strength may be one for instance, rosin size, that has but little or no wet strength itself on long soaking of the paper in water and that hence imparts very little or no wet-strength to the paper. In other words, the function of the sizing agent itself may be simply and essentially that of slowing up the rate of penetration of water into the paper, as ordinarily. In view of the fact that the invention hereof is of important utility as applied to waterleaf papers, to papers containing wet-strengthening binders, e. g., viscose, casein, etc., and to sized papers whose size content does not contribute significantly to the high wet-strength of the finished paper product hereof, it appears likely that in the case of all of these papers there is an incipient carameliza-tion or searing of the fibers and/or of the colloidal matter present in the paper under the high temperature heating treatment hereof and that such action is accompanied by the formation of wet-strengthening reaction products in the paper base; or it is possible that wet-strengthening reaction products arise in the paper base as a result of some oxidation of the fibers and/or of the colloidal matter under the high temperature heating treatment hereof. Whether or not the foregoing explanation of the mechanism underlying the wet-strengthening action in paper realized by the invention hereof is correct, it is a fact that I am enabled pursuant to the present invention to produce at low expense very valuable paper products heretofore unknown to the industry, so far as I am aware.

I claim:

1. A method of producing a paper product of high wet-strength, which comprises exposing a predried paper sheet containing, if at all, only a very small amount of binder to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

2. A method of producing a paper product of high wet-strength as a dry paper sheet is being fabricated progressively at high speed, which comprises progressively bringing the dried sheet into only momentary contact with a surface heated to about 400° to 650° F.

3. A method of producing substantially waterleaf paper of high wet-strength, which comprises exposing a predried sheet of the waterleaf paper to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

4. A method of producing sized paper of high wet-strength, which comprises exposing a predried sheet of sized paper containing only a very small amount of size to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

5. In a method involving the impregnation of fibrous sheet material with aqueous binder composition whose binder content tends to set irreversibly upon the drying of such sheet material, that step which comprises exposing the dried impregnated sheet material containing only a very small amount of the binder to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury

to such sheet material while markedly increasing its wet-strength.

6. In a method involving the impregnation of fibrous sheet material with aqueous albuminous binder composition and drying such sheet material, that step which comprises exposing the dried impregnated sheet material containing only a very small amount of such binder to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet material while markedly increasing its wet-strength.

7. In a method involving the impregnation of an interfelted fibrous sheet material with aqueous binder composition whose binder content tends to set irreversibly upon the drying of such sheet material, that step which comprises exposing the dried impregnated sheet material containing only a very small amount of the binder to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet material while markedly increasing its wet-strength.

8. In a method involving the impregnation of an interfelted fibrous sheet material with aqueous albuminous binder composition and drying such sheet material, that step which comprises exposing the dried impregnated sheet material containing only a small amount of such binder to temperatures upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet material while markedly increasing its wet-strength.

9. In a method involving the impregnation of a fibrous base with aqueous albuminous binder composition and drying such base, that step which comprises exposing the dried impregnated base containing only a small amount of such binder momentarily to a temperature of about 400° to 650° F.

10. In a method involving the impregnation of a fibrous base with aqueous albuminous binder composition and drying such base, that step which comprises exposing the dried impregnated base containing only a small amount of such binder momentarily to a temperature of about 400° to 650° F. in the presence of an insolubilizing agent for said albuminous binder.

11. In a method involving the impregnation of a paper sheet with aqueous binder composition whose binder content tends to set irreversibly upon the drying of the impregnated sheet and involving further the production of the dried impregnated paper sheet progressively and at high speed, that step which comprises progressively exposing the dried impregnated sheet containing only a small amount of such binder momentarily to intense heat and thereby to enhance the wet-strength thereof.

12. In a method involving the impregnation of a paper sheet with aqueous colloidal binder composition whose binder content tends to set irreversibly upon the drying of the impregnated sheet and involving further the production of the dried impregnated paper sheet progressively and at high speed, that step which comprises progressively exposing the dried impregnated sheet containing only a small amount of such binder to a temperature upwards of about 300° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

13. In a method involving the impregnation of a fibrous sheet with aqueous binder composition whose binder content tends to set irreversibly upon the drying of the impregnated sheet and involving further the production of the dried impregnated sheet progressively and at high speed, that step which comprises progressively bringing the dried impregnated sheet containing only a small amount of such binder into only momentary contact with a surface heated to about 400° to 650° F.

14. In a method involving the progressive impregnation of a progressively moving paper sheet with aqueous albuminous binder solution and the progressive drying of the impregnated paper sheet, that step which comprises progressively bringing the dried impregnated sheet containing only a small amount of such binder to a very high temperature for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

15. In a method involving the progressive impregnation of a progressively moving paper sheet with aqueous albuminous binder solution and the progressive drying of the impregnated paper sheet, that step which comprises bringing the dried impregnated sheet containing only a small amount of such binder into momentary contact with a surface heated to about 400° to 650° F. and thereby enhancing the wet-strength imparted thereto by said albuminous binder.

16. In a method involving the progressive impregnation of a progressively moving paper sheet with aqueous albuminous binder solution and the progressive drying of the impregnated paper sheet, that step which comprises exposing the dried impregnated sheet containing only a small amount of such binder in the presence of an insolubilizing agent for said albuminous binder momentarily to a temperature of about 400° to 650° F. and thereby enhancing the wet-strength imparted thereto by said albuminous binder.

17. A paper product which has been exposed in dried condition to a temperature upwards of about 300° F. for such a short period of time as to be substantially unscorched while being markedly improved in its wet-strength.

18. A substantially waterleaf paper product which has been exposed in dried condition to a temperature upwards of about 300° F. for such a short period of time as to be substantially unscorched while being improved markedly in its wet-strength.

19. A sized paper product which contains only a very small amount of size and which has been exposed in dried condition to a temperature upwards of about 300° F. for such a short period of time as to be substantially unscorched while being improved markedly in its wet-strength.

20. A method of producing a paper product of high wet-strength, which comprises exposing a predried paper sheet containing, if at all, only a very small amount of binder to temperatures of about 400° to 650° F. for such a limited period of time as to avoid sensible burning of or injury to such sheet while markedly increasing its wet-strength.

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