

UNITED STATES PATENT OFFICE

2,399,981

PAPER PRODUCT AND METHOD OF
MAKING THE SAMEKenneth W. Britt, Norwood, Pa., assignor to Scott
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PennsylvaniaNo Drawing. Application August 13, 1941,
Serial No. 406,727

11 Claims. (Cl. 92—40)

The present invention relates to paper having advantageous properties and to the method of making the same. By this invention, a paper may be prepared in which desired characteristics, depending on the intended use of the paper, may be imparted thereto by a simple and inexpensive method.

In the usual 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 cellulosic fibre that accounts for the strength of paper. In some instances, the dry strength, tear resistance, and other characteristics of the dry sheet are not as high as is desired, and the present invention affords a means by which these properties may be markedly increased.

In addition, the lack of wet strength of the usual paper sheet is disadvantageous in various types of paper, and is particularly marked in the case of products which during their use come into contact with moisture, for example, it is especially disadvantageous in a paper towel, the normal use of which takes place in the wet or partially wet state. The lack of wet strength results from the loss of most of the normal interfibre adhesion when the paper becomes wetted with water; for example, the usual absorbent paper retains only 5% to 10% of its dry strength when wet. The present invention provides a paper in which the interfibre adhesion or cementation in the sheet has been modified so that a paper is obtained with a high degree of wet strength and of resistance to rubbing in the wet state, as compared to an untreated paper sheet. The paper also possesses a high degree of resistance to strength loss when exposed to moist conditions for long periods of time and tends to recover any loss which it may have suffered when again restored to dry conditions.

Other desirable properties may be imparted to paper by the present invention, including increased absorbency, and decreased shrinkage and expansion when exposed to water or water vapor. The present invention also affords a means whereby a weak, porous waterleaf paper may be converted into a sheet simulating bond or parchment in appearance and feel. A paper may also be produced in accordance herewith which is both stronger and softer than a paper of the

same type not treated in accordance with the invention.

The principal object of the invention is to provide a paper whose properties are advantageously modified as hereinabove pointed out, the characteristics imparted to the paper sheet in any particular instance being dependent on the use for which the paper is intended.

Another object of the invention is to provide a paper of improved characteristics, which paper may be easily and economically prepared without the use of any toxic or other chemical detrimental in the intended use of the paper.

A further object is to provide a paper, such as towel paper, having a relatively high degree of wet strength without impairment of such properties as water-absorbency and softness required therein.

Other objects, including the provision of a novel method of preparing the product of the invention, will be apparent from a consideration of the specification and claims.

In accordance with the present invention, a paper having wet strength in excess of that inherent in the normal paper structure, and other improved properties, is provided in which the increase in wet strength is imparted to the paper by the presence of silica within and upon the surface of the fibres, said silica being distributed throughout the interfelted structure of the paper. The product is prepared by associating silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) with the interfelted structure of a paper sheet so that it is within and upon the surface of the fibres throughout the interfelted structure of the paper, and the treated paper is heated to convert the silicic acid into silica. The heating step serves to dehydrate to some extent at least the hydrophilic silicic acid and to convert it into the insoluble silica. The term "silica" is used herein to refer to the condition of the silicic acid after the paper has been dried, and is not used in a narrow sense, since the silica in the finished paper sheet may be in a somewhat hydrated form. The silicic acid is associated with the paper in such an amount that the silica, determined as SiO_2 , present in the finished paper, is sufficient to impart desirable properties such as wet strength to the paper, but in amounts insufficient to render the paper unsatisfactory for its intended purpose. It has been found that as low as 0.1% SiO_2 by weight in the finished paper based on the dry weight thereof will increase the desired properties of the finished sheet, including the wet strength thereof, to a measurable extent as com-

pared to the characteristics of the same paper not containing silica as herein described. In general, as the amount of SiO_2 present is increased, within limits, the properties of the paper are enhanced. However, due to the fact that desirable characteristics of the paper, such as the dry-tear resistance and elasticity, tend to be decreased when the SiO_2 present in the finished paper exceeds about 8%, the limits of the SiO_2 present in the paper, in accordance with the present invention, are between 0.1% and about 8% by weight, based on the dry weight of the paper.

The amount of silica employed in any particular instance will depend upon the paper treated and the properties desired in the finished product.

In the treatment of towel paper to increase its wet-strength and resistance to rubbing when wet, it is essential to maintain the normal characteristics of the paper, such as softness, for otherwise the product would not serve satisfactorily for its intended purpose. Therefore, the upper limit of SiO_2 will be controlled so that the paper is not appreciably altered in such characteristics, and the amount of SiO_2 present will generally be between 0.1% and about 3.0% by weight based on the dry weight of the paper, preferably between about 0.5% and 2.0%, generally about 1%. As will hereinafter appear, if in any particular case undesirable stiffness is imparted to the sheet by reason of the presence of the silica therein, a dispersible oil may be incorporated in the product to impart softness thereto.

The present invention is to be differentiated from the silicate sizing process, wherein sodium silicate solution is added to the dilute pulp-water suspension in the beater, followed by the addition of alum. The alum and sodium silicate react to form a precipitate, a portion of which adheres to the surfaces of the fibres, without significant penetration thereof. In accordance with the present invention, the paper after its formation into an interfelted web is treated in such a manner that silicic acid is incorporated within, as well as upon the surface of the fibres in controlled amounts to impart to the paper the desirable characteristics. The incorporation of the silicic acid within and upon the surface of the fibres, as herein contemplated, produces a sheet that, upon drying, has silica deposited within the fibres which reduces their tendency to swell upon the application of water and otherwise functions to impart the desirable properties described.

The paper treated in accordance with the invention may be of any type or grade, for example, towel, waterleaf, kraft, bond, wall board, building paper, outdoor advertising paper, photographic paper, wrapping paper, and the like.

As previously stated, silicic acid is associated with the interfelted structure of the paper so that it is within and upon the surface of the fibres thereof, and the treated sheet is heated to convert the silicic acid into silica. The silicic acid may be associated with the paper by several methods, for example, by treating the paper with an aqueous solution of silicic acid, or by treating the paper with a solution of an alkali metal silicate, with subsequent neutralization, either before or after drying, of the alkali metal oxide associated with the SiO_2 of the alkali metal silicate, so that there is no sodium silicate present, that is, no sodium oxide associated with the SiO_2 . As a result of the neutralization, a siliceous product is formed, which for the purposes

of the present invention is deemed to be silicic acid.

The impregnating solution is brought into contact with the paper either during its fabrication or after it has been fabricated and dried. Advantageously, the solution is applied to the paper while the paper sheet is being processed, and the solution may be brought into contact with the paper sheet at any stage, after the formation of the interfelted fibre web and prior to the completion of the drying thereof, where sufficient water has been removed to permit absorption of the solution by the sheet. Preferably, the treatment with the impregnating solution takes place when the moisture in the sheet has been reduced to about 30%, or below, and, therefore, at a suitable point in the drier section. The passage of the paper over the remaining driers will be sufficient to dry the paper and to deposit the chemical within and upon the surface of the fibres. In the case the solution employed is a solution of silicic acid or in the case paper has been treated with sodium silicate solution followed by treatment with the acidic material prior to drying the paper, silicic acid is deposited in the paper which is converted to silica upon drying. As will hereinafter be discussed further, in the event the acid treatment is not carried out until after the paper is dried, alkali metal silicate will be deposited within and upon the surface of the fibres prior to the treatment with the acidic material. In the case a dried paper sheet is treated with the impregnating solution, the sheet after treatment with the solution of silicic acid or with the solution of alkali metal silicate followed by the acid treatment may be dried in any desired manner by subjecting it to a temperature above 212°F . and below the temperature at which the paper is damaged, for example, at 250°F . to 300°F ., in a drying chamber or by passing it over a heated roll or through a heated calender.

The paper sheet, whether treated during the paper-making process or after drying, may be brought in contact with the solution (or solutions) by any suitable means in order to impregnate the paper. For example, it may be applied by means of a size press such as is used in the conventional tub sizing process. Alternatively, it may be sprayed upon the moving sheet of paper by means of a spraying device.

An aqueous solution of an alkali metal silicate is used in the preparation of the silicic acid solution if the paper is to be treated therewith and is used to impregnate the paper in the process where subsequent treatment with acid forms the silica in the paper sheet. The solution has been designated herein as an alkali metal silicate solution which includes both potassium and sodium silicate, but since the sodium silicate solutions are more economical for use, the invention will be described hereinafter using sodium silicate as typical. While a solution of any desired ratio of Na_2O to SiO_2 , where the molecular ratio of SiO_2 exceeds that of Na_2O , for example, solutions having a molecular ratio of Na_2O to SiO_2 between 1 to 3.8 and 1 to 2, may be employed, the use of a solution relatively low in alkalinity is preferred, since less acid is required for its neutralization. In addition, in the process in which the paper is impregnated with the sodium silicate solution, prior to the acid treatment, it is possible by the use of a solution relatively low in alkalinity to associate a larger amount of SiO_2 with the paper without encountering difficulties due to excessive

alkalinity. For these reasons, a solution containing a molecular ratio of Na_2O to SiO_2 of 1 to 3.8 or 1 to 3.3, such solutions now being available in the market, will usually be employed. If desired, the solution, however, may be prepared by dissolving solid soluble sodium silicate in the appropriate amount of water. In the process in which the paper is impregnated with sodium silicate prior to the acid treatment, a sodium silicate solution having relatively high alkalinity may be adjusted to the desired alkalinity by the addition of appropriate acidic material.

In the preferred method, the paper sheet is treated with a solution of silicic acid. The silicic acid solution may be prepared by adding a diluted alkali metal silicate solution to a dilute solution of an acidic material sufficient in amount to neutralize the alkali, and to produce a solution of the desired acidity and concentration. The choice of acidic material for reaction with the silicate is not important, and among the materials available for use, the following may be mentioned: hydrochloric, sulphuric, nitric, phosphoric, acetic, formic, oxalic, and lactic acids, and sodium bisulphate. Mixtures of acids may be employed, if desired. Very satisfactory results are obtained if sulphuric or hydrochloric acid, or a mixture of hydrochloric and acetic acids, is employed.

In the preparation and use of the silicic acid solutions, care must be taken to prevent gelation. The time of gelation is dependent principally upon the pH value of the solution, the concentration of silicic acid and the temperature. On the acid side of the neutral point, the higher the pH, the more rapid the gelation; also the higher the concentration or the temperature, the more rapid is the gelation. The pH value of the solution applied to the paper should not be so low that a detrimental effect upon the cellulosic fibre results, and the concentration of solution and the amount of solution applied to the paper must be so adjusted as to deposit the desired amount of silica in the paper. An additional reason for employing a solution of only mild acidity resides in the fact that, in most instances it will be desirable to provide a finished paper which is only slightly acid, for example, a paper with a pH value between about 3 and 6.5, preferably between 4.0 and 6.0, as determined by applying to the dry paper drops of standard La Motte indicator solutions and noting the color.

In view of these facts, the range of pH of the solution as applied to the paper should be from about 2 to 5, preferably between 2.5 and 3.5, and the concentration of silicic acid should not exceed about 10%, figured as SiO_2 and generally above 1%, preferably between 4.0% and 7.0%. The solution of silicic acid should be maintained at temperatures below about 30°C . It is understood that the higher concentrations of silicic acid are used in conjunction with the lower pH values, while the higher pH values may be safely used only with the lower concentrations of silicic acid.

There are three methods that may be employed in handling the silicic acid solutions: (1) the preparation in advance of a quantity of silicic acid solution suitable for application to the paper; (2) the metering together continuously of acid and silicate solutions of suitable concentration immediately before application to the paper; and (3) the preparation of a relatively stable silicic acid solution of pH value of 1.0 to 2.0 and the metering of this solution with sufficient silicate solution immediately before application to

the paper to raise the pH to the desired point for such application. It is important to have rapid and complete mixing during the preparation of the silicic acid solution.

In the first case, the upper safe limit of silicic acid concentration is about 5% and the preferable range is from 2% to 4%, and the pH range is preferably from 3 to 4. In the preparation of the silicic acid solution, it is desirable to add the diluted sodium silicate solution to the dilute acid, rather than the reverse. Again, it is understood that the higher concentrations are preferably used with the lower pH values, while the higher pH values may be safely used with the lower concentrations. In the use of this procedure, the amount of solution applied to the paper will generally be large, since otherwise only very small amounts of silica would be deposited in the paper.

In the second case, the pH value of the mixture of acid and silicate is preferably about 2.5 to 3.5, and the concentration of silicic acid may be as high as 10%, or even higher, preferably about 4% to 7%. It is seen that in this case the amount of solution applied to the paper may be relatively small, since the higher concentration permits the deposition of relatively large amounts of silica that will occur even with relatively small amounts of solution.

In the third case, the very acidic silicic acid solution, pH 1.0 to pH 2.0, may be prepared in concentrations as high as about 8%, and a silicate solution or suitable buffer solution is metered into this solution to form a solution of the desired pH value and concentration. The final mixture as applied to the paper will conform to the limits given under the second method.

In all cases, it is advantageous to keep the temperature of all solutions as low as feasible. For example, after the preparation of dilute sulphuric acid, it is advantageous to allow the heat produced by the dilution to dissipate before the addition of the silicate. In some instances, it may be desirable, in order to prevent gelation, to refrigerate the solution to a temperature below room temperature, and, even to a temperature only slightly above the freezing point of the solution.

In the modification of the process where the paper is treated with a solution of an alkali metal silicate with subsequent neutralization, preferably by treatment with acid, to precipitate the silica, the concentration of the silicate solution is relatively unimportant so long as the solution is sufficiently dilute to be absorbed by the paper, an example of a range of concentrations (solid sodium silicate in solution) which may be employed being from .5% to 10%, preferably from 2 to 4%, although it is to be understood that solutions of other concentrations may be used.

Preferably, the treatment with acid follows the treatment with the silicate solution without any intermediate drying step, for in such case the precipitation of silicic acid within and upon the surface of the fibres of the interfelted web takes place rapidly and completely. If desired, however, the paper after its treatment with the silicate solution may be dried and subsequently the acid solution applied. For example, a paper containing sodium silicate, with or without silica, within and upon the surface of the fibres may be treated with an acidic material to neutralize the sodium silicate, the amount of siliceous material in the paper providing the silicic acid, and,

upon drying, the silica required to give the desired characteristics to the paper. The amount and concentration of the acid solution applied depends on the alkalinity of the paper following the treatment with the silicate solution, and sufficient acid is added to convert the alkali metal silicate into silicic acid, but in order not to damage the cellulose fibre and to provide a paper of relatively low acidity, the use of a large excess of acid is avoided. Any acidic material may be employed and those hereinbefore mentioned for use in the preparation of the silicic acid solution are typical examples, but organic acids, such as acetic or formic, have been found to be most advantageous. For example, the concentration of the acid, in the case of acetic acid, will be between .2% and 6.0%. As previously stated, the acid may be applied in any desired manner, for instance, by a tub sizing step or by spraying.

An alternative, but less preferable, method of neutralizing the Na_2O associated with the SiO_2 of the sodium silicate resides in the incorporation in the paper of an ammonium salt, such as ammonium chloride, ammonium sulphate, or diammonium phosphate, the latter being preferred, and the subsequent heating of the paper to volatilize ammonia, with the subsequent conversion of the silicate into silicic acid, and finally into silica. The ammonium salt is preferably incorporated in the paper simultaneously with the incorporation of the sodium silicate, but the paper may be impregnated with the solution of the ammonium salt prior or subsequent to its impregnation with the sodium silicate solution.

In my copending application, Serial No. 402,728, filed even date herewith, the production of a paper containing an alkali metal silicate, or an alkali metal silicate together with silica, within and upon the surface of the fibres is described and claimed. The present invention is to be distinguished therefrom, since, in accordance herewith, silica and not alkali metal silicate is present within and upon the surface of the fibres of the paper, and in accordance with this invention, silica is the only silica-containing material present in the paper in a sufficient quantity to contribute materially to the wet-strength of the paper. The invention of this application, as previously pointed out, contemplates the deposition of silica within and upon the surface of the fibres, and it is possible to accomplish this result by the use of a silicic acid solution or by the subjection of paper containing alkali metal silicate to neutralization to form silicic acid. Subsequent heating in both cases converts the hydrophilic silicic acid into silica.

The properties of the product of the present invention, whether made by employing a silicic acid solution or a sodium silicate solution with subsequent treatment with acid, may be further modified by the incorporation therein of other materials such as starch, glue, and vegetable gums. If desired, additional softness may be imparted to the paper by the incorporation therein of a dispersible oil, for example, of the type known as a textile finishing oil. The term "dispersible oil" as used herein and in the claims includes those oils which, either through their emulsifiable or soluble properties, are capable of being dispersed in an aqueous medium. A paper containing silica within and upon the surface of the fibres, if treated with these oils, within the practical limits hereinafter set forth, is considerably softened and yet retains a strength, both in the wet and dry state, substan-

tially greater than that of a similar paper so treated which does not contain silica. Since the use of the dispersible oil tends to cause a decrease in the strength of the paper, the amount thereof associated with the paper will be kept below the point where the increase in strength imparted by the silica will be unduly reduced by the oil. Satisfactory results are obtained by using about .1% to .5% of oil by weight based on the dry weight of the paper, and the use of amounts higher than this and up to about 3%, or even higher, may be used if desired, depending on the type of paper, the amount of silica associated therewith, and the results to be obtained. The dispersible oil may advantageously be applied to the paper by spraying on the paper or by dispersing it in the solution (or solutions) with which the paper is treated, or in any other suitable manner.

The following examples are illustrative of the process:

Example I

100 parts of a 10% sodium silicate solution in which the proportion of SiO_2 to Na_2O is 3.8 to 1 is added gradually to 20 parts of a 10% hydrochloric acid solution in 140 parts of water. The resulting solution contains about 3.5% silicic acid and has a pH value of about 3. Towel paper weighing 34 pounds per ream prepared from 65% unbleached sulphite pulp and 35% mechanical wood pulp is sprayed or otherwise impregnated with this solution to a moisture content of approximately 20%. The paper is then thoroughly dried at a temperature of about 2500° F. and the finished paper contains .875% SiO_2 . The wet strength of the paper is increased to 3 to 4 times over that of the original paper, and the other characteristics of the paper, such as absorbency and dry tensile strength, are improved. The paper retains its softness and other properties required in a towel paper.

Example II

100 parts of a 10% sodium silicate solution in which the proportion of SiO_2 to Na_2O is 3.8 to 1 is added gradually to 20 parts of a 10% hydrochloric acid solution in 30 parts of water. The resulting solution contains about 6% silicic acid and has a pH value of about 3.0. This solution is applied to towel paper made from 50% bleached sulphate pulp and 50% unbleached sulphite pulp at a point in the paper machine drier section at which the paper contains approximately 30% water content. The amount of silicic acid solution applied is 15% of the dry weight of the fibre and the weight of SiO_2 retained by the paper is approximately 0.7% of the fibre. The paper is then thoroughly dried by continuing its passage through the drier section at a temperature of about 300° F. The wet strength of the paper is increased 3 or 4 times over the original paper, and the other characteristics of the paper, such as absorbency and dry tensile strength, are improved. The paper retains its softness and other properties required in a towel paper.

Example III

A waterleaf uncreped paper made from 100% bleached pulp of high alpha content is impregnated with a silicic acid solution of 4% concentration and a pH of 3.5, the amount of solution taken up by the paper being about 50% of the dry weight of the fibre. The amount of SiO_2 retained by the paper is 2%. The wet tensile

strength is approximately 9 times that of the untreated paper, and is greatly increased in stiffness, rubbing resistance, and surface hardness and resembles a good grade of bond paper in feel and appearance.

Example IV

Two parts of a dispersible oil (Socony Vacuum Company's "Textile finishing oil B") are added to the silicic acid solution of Example I and the paper is treated as set forth in that example. The finished paper contained 0.8% dispersible oil and was appreciably softer than the paper obtained by Example I. The wet strength of the paper, however, was not materially diminished.

Example V

A 5% solution of sodium silicate containing a ratio of Na_2O to SiO_2 of 1 to 3.8 is applied by spraying or otherwise to towel paper weighing 34 pounds per ream prepared from 65% unbleached sulphite pulp and 35% mechanical wood pulp at a point in the paper machine drier section at which the paper contains approximately 30% water. The amount of sodium silicate solution applied is 20% of the dry weight of the fibre. The paper as soon thereafter as convenient and prior to appreciable further drying thereof is treated by spraying or otherwise with a 3% solution of acetic acid, the acid solution application being 20% of the dry weight of the fibre. The paper is then thoroughly dried by continuing its passage through the drier section at a temperature of about 300° F. The weight of silica figured as SiO_2 retained by the paper is approximately 0.8% of the fibre. The paper had properties similar to those given above in Example II.

Example VI

In this example, the paper is treated with the sodium silicate solution in the manner described in Example V and the paper is thereafter dried by continuing its passage through the drier section before treatment with acid. A 3% acetic acid solution is then applied to the dried paper by spraying or otherwise, the amount of acid applied being 20% of the dry weight of the fibre. The paper as in Example V contains approximately 0.8% of silica figured as SiO_2 and the paper had characteristics similar to those described in Example II.

The following tables illustrate the properties of paper of the present invention containing different amounts of silica incorporated therein by using a silicic acid solution. In Tables I to V, inclusive, the paper treated was a towel paper weighing 38 pounds per ream prepared from 50% bleached sulphate pulp and 50% unbleached sulphite pulp.

Table I.—Wet tensile strength

The wet tensile strength was determined on a Schopper tensile machine and the results are in pounds tensile (machine direction) required to break a strip of wet paper 15 mm. wide.

Percentage of SiO_2 present	Wet tensile strength
0	0.20
0.6	0.57
1.24	0.87
2.46	1.11
4.90	1.62
7.50	2.03

Table II.—Porosity

The porosity was determined by a Gurley porosity tester and the figures are expressed in seconds required to pass 300 cc. of air.

Percentage of SiO_2 present	Number of seconds
0	15
1.24	15
2.46	13.3
4.90	11.7
7.50	13.3

These figures indicate that no appreciable change in porosity is encountered with the given percentages of silica.

Table III.—Tearing strength

The dry-tearing strength was determined by an Elmendorf tearing tester and the results are expressed in grams force required to tear 4.3 cm. of paper.

Percentage of SiO_2 present	Tearing strength
0	81.2
0.9	97.0
1.24	106
2.46	102
4.90	110
7.50	83.4

This table shows that when amounts of SiO_2 less than about 8% are present in the paper, the tearing strength is increased. When larger amounts of SiO_2 are present, the tearing strength tends to be decreased below the original paper; for example, at 10.9% SiO_2 , the tearing strength is 73.4.

Table IV.—Stiffness

The stiffness was measured by a Clark softness tester as described in Paper Trade Journal, March 28, 1935, and the results are expressed as $\text{WL}^3/10^3$, in which W is the basis of the paper in grams per square meter and L is the critical length as determined by the instrument.

Percentage of SiO_2 present	Stiffness
0	25.8
0.7	28.3
1.24	32.4
2.46	34.6
4.90	85.0
7.50	101.0

Table V.—Dry tensile strength

The dry tensile strength was determined on a Schopper tensile machine, and the results are in pounds tensile (machine direction) required to break a strip of dry paper 15 mm. wide.

Percentage of SiO_2 present	Dry tensile strength
0	2.10
1.24	2.16
2.46	2.24
4.90	3.12
7.50	3.75

Table VI

In the following table, the paper was a towel paper weighing 34 pounds per ream prepared from 65% unbleached sulphite pulp and 35% mechanical wood pulp. The effect of the use of a

softening oil (Socony Vacuum Company's "Textile finishing oil B") on the physical characteristics of a paper is illustrated, the figures given being determined as set forth in connection with the other tables:

Per cent SiO ₂	Per cent oil	Dry tensile	Wet tensile	Stiffness WL %/10 ²
0	0	2.38	0.25	37.7
2.7	0	2.80	1.47	44.5
2.7	0.18	3.01	1.48	37.2
2.7	0.36	2.48	1.22	34.2
2.7	0.72	2.40	1.08	30.2
2.7	1.44	2.44	0.99	27.3

While the above tables set forth figures obtained by using towel paper, corresponding changes in properties are obtained to more or less the same extent in other types of paper. It will be seen that in accordance with the present invention, the amount of SiO₂ incorporated in the paper sheet will be determined in any particular case by the characteristics it is desired to impart to the product.

Considerable modification is, therefore, possible in the amount of SiO₂ present in the paper, as well as in the method employed in depositing the silica within and between the fibres of the interfelted web, without departing from the essential features of the invention.

I claim:

1. A paper having increased wet strength and substantially unimpaired dry tear resistance, and having heat-treated silica within and upon the surface of the fibres throughout the interfelted structure of said paper and present in an amount between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper, the said silica being the only silica-containing material present in sufficient quantity to contribute materially to the wet-strength of the paper.

2. A paper having increased wet strength and substantially unimpaired dry tear resistance, and having heat-treated silica within and upon the surface of the fibres throughout the interfelted structure of said paper and present in an amount between 0.1% and about 3% SiO₂ by weight based on the dry weight of the paper, the said silica being the only silica-containing material present in sufficient quantity to contribute materially to the wet-strength of the paper.

3. A towel paper having increased wet strength and substantially unimpaired dry tear resistance, and having heat-treated silica within and upon the surface of the fibres throughout the interfelted structure of said towel paper and present in an amount between approximately 0.5% and about 2% SiO₂ by weight based on the dry weight of the paper, the said silica being the only silica-containing material present in sufficient quantity to contribute materially to the wet-strength of the paper.

4. The method of increasing the wet strength of paper while preserving substantially the dry tear resistance thereof, which comprises associating within and upon the surface of the fibres throughout the interfelted structure of said paper silicic acid in an amount sufficient to furnish between 0.1% and about 8% SiO₂ by weight based upon the dry weight of the paper, the said silica being the only silica-containing material present in sufficient quantity to contribute materially to the wet strength of the paper, and heating said paper to convert said silicic acid into silica, with-

in and upon the surface of the fibres throughout the interfelted structure of said paper.

5. The method of increasing the wet strength of paper while preserving substantially the dry tear resistance thereof, which comprises impregnating paper with a solution of silicic acid in an amount sufficient to furnish between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper at a point in the production of said paper after the formation of the interfelted web and prior to the completion of the drying thereof, and heating said paper to dry it and to convert said silicic acid into silica distributed within and upon the surface of the fibres throughout the interfelted structure of the paper.

6. The method of increasing the wet strength of paper while preserving substantially the dry tear resistance thereof which comprises impregnating paper with a solution of sodium silicate, impregnating said paper with a solution of an acidic material to convert the sodium silicate absorbed by the paper into silicic acid, said solution of sodium silicate furnishing between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper, and heating said paper to convert said silicic acid into silica distributed within and upon the surface of the fibres throughout the interfelted structure of the paper.

7. The method of increasing the wet strength of paper while preserving substantially the dry tear resistance thereof which comprises impregnating paper with a solution of sodium silicate, impregnating said paper with a solution of an acidic material to convert the sodium silicate absorbed by the paper into silicic acid, said solution of sodium silicate furnishing between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper, said impregnating steps being conducted at a point in the production of said paper after the formation of the interfelted web and prior to the completion of the drying thereof, and heating said paper to dry it and to convert said silicic acid into silica distributed within and upon the surface of the fibres throughout the interfelted structure of the paper.

8. The method of increasing the wet strength of paper while preserving substantially the dry tear resistance thereof, which comprises impregnating paper with a solution of silicic acid in an amount sufficient to furnish between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper, and heating said paper to convert said silicic acid into silica distributed within and upon the surface of the fibres throughout the interfelted structure of the paper.

9. The process of claim 8 in which the solution of silicic acid with which the paper is impregnated has a pH value between about 2 to 5.

10. The process of claim 8 in which the solution of silicic acid with which the paper is impregnated has a pH value between about 2.5 and 3.5.

11. The method of obtaining a paper product of high wet-strength and substantially normal dry tear resistance which comprises neutralizing a paper containing an alkali metal silicate in an amount providing between 0.1% and about 8% SiO₂ by weight based on the dry weight of the paper upon neutralization, said silicate being distributed within and upon the surface of the fibres throughout the interfelted structure of said paper, and heating said paper to convert the silicic acid formed upon neutralization into silica.

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