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PAPER PRODUCT AND METHOD OF MAKING SAME

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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. One of the outstanding characteristics, however, of the normal interfibre adhesion in a sheet of paper is the loss of most of this adhesive strength when the sheet of paper becomes wetted with water. Thus, the usual absorbent paper retains only 5% to 10% of its dry strength, when wetted with water. The lack of wet strength is disadvantageous in the various types of paper, but 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. In such a product, it is, of course, essential that its characteristics, such as absorbency, porosity and softness be retained, for otherwise the product would not serve satisfactorily for its intended purpose.

The principal object of the present invention is to provide a paper, in which the interfibre adhesion or cementation in the sheet has been modified so that said bonding retains an appreciably greater degree of strength when wetted.

A further object of the invention is to provide a paper having a relatively high degree of wet-strength without substantial impairment of such properties as water absorbency and softness required in certain classes of paper, which paper may be easily and economically prepared without the use of any toxic or other chemical disadvantageous in the intended use of the paper.

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 an alkali metal silicate (alkali metal oxide associated with silica) within and upon the surface of the fibres, said alkali metal silicate being distributed throughout the interfelted structure of the paper. The increase in wet-strength may be due to the presence of the alkali metal silicate alone, or to the presence of the alkali metal silicate together with silica derived therefrom. The purpose of converting a portion of the alkali metal silicate into silica is to provide a product with reduced alkalinity. The product is prepared by impregnating paper with a solution of an alkali metal silicate with or without treatment with a substance causing the conversion of a portion of the alkali metal silicate into silicic acid during the process, and by heating the impregnated paper to deposit the alkali metal silicate or the alkali metal silicate and silica within and upon the surface of the fibres throughout the interfelted structure of the paper.

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, the invention is particularly applicable for the treatment of towel paper and other papers, the normal use of which takes place in the wet or partially wet state.

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 surface of the fibres, without penetration thereof. In accordance with the present invention, the paper after its formation into an interfelted web is treated with the alkali metal silicate solution which is absorbed by the fibres themselves, so that upon drying of the product, alkali metal silicate, or alkali metal silicate together with silica, is deposited within, as well as upon the surface of the fibres, reducing their tendency to swell upon the application of water.

As previously stated, the paper, either before or after drying, is treated with the alkali metal silicate solution. 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, where sufficient water has been removed to permit absorption of the solution by the sheet. Preferably, the treatment with the solution takes place when the moisture in the sheet has been

reduced to about 30% or below, and, therefore, as the paper sheet leaves the intermediate driers. The passage of the paper sheet over the remaining drier section will be sufficient to dry the paper and to deposit alkali metal silicate, or the alkali metal silicate and silica, in at least a partially dehydrated form within and upon the surface of the fibres, so that the tendency of paper fibres to swell upon the application of water will be reduced. In the case a dried paper sheet is treated with the solution, the sheet 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 into contact with the alkali metal silicate solution 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 the paper by means of a spraying device.

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 solutions as typical. While a solution of any desired ratio of Na_2O to SiO_2, where the molecular proportion of SiO_2 exceeds that of Na_2O, for example, solutions having a molecular ratio of Na_2O to SiO_2 between about 1 to 3.8 and 1 to 2, may be employed, the use of a solution relatively low in alkalinity is preferred, since it is thus possible to associate a larger amount of sodium silicate with the paper without raising the alkalinity of the paper to an undesirable point. For example, 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, or a sodium silicate solution having relatively high alkalinity may be adjusted to the desired alkalinity by the addition of appropriate acidic material. The sodium silicate concentration in the 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 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. In the treatment of paper where it is desired to maintain a light color, the concentration of the solution of alkali metal silicate should be below that point where appreciable discoloration, due to excessive alkali, is encountered. In the case of paper of the type treated in Example IV, it has been found that concentrations above about 4% tend to cause discoloration.

The amount of sodium silicate, or of sodium silicate and silica, deposited within and upon the surface of the fibres of the interfelted web and present in the dried product depends upon the particular use for which the paper is intended. Whether the sodium silicate is present alone or with silica, the amount of sodium silicate will be at least 0.1% and will not exceed about 2.5%, and preferably will not exceed about 1.6%, figured as SiO_2, by weight based on the dry weight of the paper. The presence of more than about 2.5% of sodium silicate (figured as SiO_2) tends to produce undesirable properties in the paper, such as discoloration, odor and causticity. The presence of silica with sodium silicate produces an improvement in certain paper properties which cannot be obtained with sodium silicate alone, due to excessive alkalinity. In the event that silica is present with the sodium silicate, the amount thereof is preferably equal to or less than that of the sodium silicate, but the amount of silica may, if desired, exceed that of the sodium silicate. 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 total sodium silicate and silica present in the finished paper exceeds about 8% (figured as SiO_2), the upper limit of the sodium silicate and silica present in the paper, in accordance with the present invention, is about 8% (figured as SiO_2) by weight based on the dry weight of the paper. The amount of sodium silicate and silica employed in any particular instance will depend upon the paper treated and the properties desired in the finished product. Herein, and in the claims, the term heat-treated material selected from the group consisting of an alkali metal silicate and a mixture of an alkali metal silicate and silica refers to the sodium silicate and/or the mixture of sodium silicate and the silica derived therefrom present in the paper, in accordance with the present invention.

In the treatment of towel paper to increase its wet strength and resistance to rubbing, when wet, it is essential to obtain 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 sodium silicate, or of sodium silicate and silica, will be controlled, so that the paper is not appreciably altered in such characteristics, and the amount thereof will generally not be above about 3.0% (figured as SiO_2) by weight based on the dry weight of the paper, preferably between 0.5% and 2.0%, generally about 1% (figured as SiO_2). Advantageously, the heat treated material is made up of approximately equal parts of sodium silicate and silica. As will hereinafter appear, if in any particular case undesirable stiffness is imparted to the sheet by reason of the presence of the siliceous material therein, a dispersible oil may be incorporated in the product to impart softness thereto.

Several methods are available for accomplishing the conversion of a portion of the sodium silicate into silica, it being understood that in accordance with this invention there is always present at least 0.1% sodium silicate in the paper. For example, an acidic material may be added to the sodium silicate solution in sufficient amounts to result in the deposition of silica, together with the sodium silicate, upon the drying of the paper. If this method is followed, the acidic material should not cause the formation of a precipitate in the impregnating solution. Another method resides in the subjection of the paper, after impregnation, with the sodium silicate solution, to treatment with an acidic material, the amount of acidic material employed being insufficient to neutralize all of the sodium silicate. Preferably, the treatment with acid follows the treatment with the silicate solution without any intermediate drying step. 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 within and upon the surface of the fibres may be treated with an acidic material to neutralize a portion of the sodium silicate. In the methods involving the treatment with acidic material, such material may be an inorganic or organic acid, or an acid salt. For example, hydrochloric, sulphuric, nitric, phosphoric, acetic, formic, oxalic or lactic acid, or sodium bisulphate. Mixtures of acids may be employed if desired.

Another method of providing silica with the sodium silicate within and upon the surfaces of the fibres involves the incorporation of an ammonium salt in the paper prior to the drying thereof. The ammonium salt, such as diammonium phosphate, ammonium chloride or ammonium sulphate, may be present in the sodium silicate solution and thus absorbed by the paper with the sodium silicate. The presence of the ammonium salt results in reduced alkalinity of the paper treated with the silicate due to the volatilization of ammonia during the drying operation, with consequent conversion of a portion of the silicate into silica. Instead of using the ammonium salt in the solution of sodium silicate, the paper may, if desired, be treated with a solution of the ammonium salt either before or after its treatment with the sodium silicate solution, but this method is not preferred, since it has no advantages over the use of a solution containing both the sodium silicate and the ammonium salt. Generally, it is not practicable to produce a paper containing more than about 5% free silica by the use of ammonium salts.

When an ammonium salt is used with sodium silicate, in order to reduce the alkalinity of the finished product, the amount of such ammonium salt employed is less than that necessary to completely neutralize the sodium silicate, i. e., the number of ammonium radicals so introduced is less than the sodium atoms contained in the sodium silicate. Accordingly, the weight of the ammonium salt in proportion to the sodium silicate will depend upon the alkalinity of the silicate and upon the particular ammonium salt employed as illustrated by the following tables. The treated paper, therefore, will contain some soda (Na_2O) still associated with silica.

Table I

Diammonium phosphate, per cent of silicate by weight	Column A, ratio of sodium atoms to ammonium radicals	Column B, ratio of sodium atoms to ammonium radicals
10	100:22	100:20
20	100:44	100:40
30	100:66	100:60
40	100:88	100:80
50	100:110	100:100

Table II

Ammonium chloride, per cent if silicate by weight	Column A, ratio of sodium atoms to ammonium radicals	Column B, ratio of sodium atoms to ammonium radicals
10	100:27	100:24
20	100:54	100:48
30	100:81	100:72
40	100:108	100:96
50	100:135	100:120

In the above tables, Column A shows the results when the silicate employed has a ratio of 1 Na_2O to 3.8 SiO_2, and Column B shows the results when the silicate employed has a ratio of 1 Na_2O to 3.3 SiO_2. It is seen from these tables that the amount of diammonium phosphate employed in combination with sodium silicate of said 1–3.8 ratio will be less than about 45% by weight of the sodium silicate, and with sodium silicate of said 1–3.3 ratio, the amount will be less than about 50%. In the case of ammonium chloride, the amount of ammonium salt for the two kinds of silicate above referred to will be less than about 37% and about 42%, respectively.

Another material that may be employed with the sodium silicate-containing paper, irrespective of the presence of the ammonium salt, is 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. These oils produce a softening effect on paper treated with sodium silicate solution, which effect is not encountered to the same extent with paper which has not been treated with the sodium silicate solution. Since the use of the dispersible oil tends to cause a decrease in wet strength, the amount thereof associated with the paper will be kept below the point where the increase in wet-strength imparted by the sodium silicate will be appreciably 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. The dispersible oil may be applied to the paper, either by dispersing it in the sodium silicate solution (the preferred mode of operation) or by treating the paper with a solution of the dispersible oil either before or after its treatment with the sodium silicate solution.

Since the product of the present invention contains sodium silicate, it is to be distinguished from the product of my copending application, Serial No. 406,727, filed even date herewith, in which silica, but no sodium silicate, is deposited within and upon the surface of the fibres of the interfelted structure.

The following examples are illustrative of the process, the wet tensile strength figures set forth being determined on a Schopper tensile machine, the results being given in pounds tensile (machine direction) required to break a strip of wet paper 15 mm. wide:

Example I

An air-dried towel paper, weighing 38 pounds per ream prepared from 50% bleached sulphate and 50% unbleached sulphite pulps is treated with a 2% solution of sodium silicate (3.8 SiO_2 to 1 Na_2O), the amount of solution applied being 40% of the weight of the paper treated. The paper is dried by heating it to a temperature in the neighborhood of 275° F., and contains 0.8% sodium silicate (dry basis). The wet tensile strength of the untreated paper is 0.25 pound as compared to 0.75 pound for the processed paper.

Example II

An air-dried towel paper of the grade used in Example I is treated with a solution containing 3% sodium silicate (3.8 SiO_2 to 1 Na_2O), and 1% Socony-Vacuum Company's "Textile finishing oil

B," the amount of solution applied being 20% of the weight of the paper treated. The paper is dried by heating it to a temperature in the neighborhood of about 300° F., and contains 0.6% sodium silicate and 0.2% dispersible oil (dry basis). The wet tensile strength of the untreated paper is 0.25 pound, as compared to 0.50 pound for the processed paper.

Example III

An air-dried towel paper of the grade used in Example I is treated with a solution containing 4% sodium silicate (3.8 SiO_2 to 1 Na_2O) and 1% diammonium phosphate, the amount of solution applied being 30% of the weight of the paper treated. The paper is dried by heating it to a temperature of about 250° F. and contains .54% sodium silicate, .53% silica (.96% sodium silicate and silica figured as SiO_2) and .3% of phosphate figured as diammonium phosphate (all on a dry basis). The wet tensile strength of the untreated paper is 0.25 pound, as compared to 1.00 pound for the processed paper.

Example IV

100 pounds of towel paper (dry basis) weighing 34 pounds per ream prepared from 65% unbleached sulphite and 35% mechanical wood pulps, containing 30 pounds of water as it travels between the intermediate and final drier sections is passed through a solution containing 4% sodium silicate (3.8 Na_2O to 1 SiO_2), 0.6% diammonium phosphate, and .2% dispersible oil used in Example II, the amount of solution applied being 20 pounds. The paper is dried by passing it over the final drier section at the usual temperature maintained therein and contains 0.54% sodium silicate, .21% silica (.63% sodium silicate and silica figured as SiO_2), 0.12% phosphate figured as diammonium phosphate, and 0.04% dispersible oil. The wet tensile strength of the untreated paper is 0.25 pound, as compared to .75 pound for the processed paper.

The properties of the product of the present invention may be further modified by the incorporation therein of other materials, such as starch, glue and vegetable gums.

Considerable modification is possible in the methods of processing, as well as in the amounts of alkali metal silicate and other materials (if any), incorporated in the paper without departing from the essential features of my invention.

I claim:

1. A paper having increased wet-strength and substantially unimpaired dry tear resistance, and having heat-treated material selected from the group consisting of an alkali metal silicate and a mixture of an alkali metal silicate and silica, reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of said paper, said heat-treated material being present in an amount between 0.1% and about 8%, figured as SiO_2, by weight based on the dry weight of the paper, at least a portion of said heat-treated material being alkali metal silicate present in an amount not exceeding about 2.5%, figured as SiO_2 based on the dry weight of the paper.

2. A paper having increased wet-strength and substantially unimpaired dry tear resistance, and having heat-treated sodium silicate reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of said paper and present in an amount between .01% and about 2.5% figured as SiO_2, by weight based on the dry weight of the paper, said sodium silicate being the only siliceous material present in sufficient quantity to contribute materially to the wet-strength of the paper.

3. A paper having increased wet-strength and substantially unimpaired dry tear resistance, and having heat-treated sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper and present in an amount less than about 8%, figured as SiO_2, by weight based on the dry weight of the paper, the sodium silicate being present in an amount between 0.1% and about 2.5%, figured as SiO_2, by weight based on the dry weight of the paper.

4. A towel paper having increased wet-strength and substantially unimpaired dry tear resistance. and having heat-treated sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper and present in an amount between approximately .5% and 2.0%, figured as SiO_2, by weight based on the dry weight of the paper, the sodium silicate being present in an amount between 0.1% and about 1%, figured as SiO_2, by weight based on the dry weight of the paper.

5. The method of increasing the wet-strength of paper while preserving the dry tear resistance thereof, which comprises associating within and upon the surface of the fibres throughout the interfelted structure of said paper a heat-treated material selected from the group consisting of an alkali metal silicate and a mixture of an alkali metal silicate and silica, reducing the tendency of the paper fibres to swell upon the application of water, in an amount between 0.1% and about 8%, figured as SiO_2, by weight based on the dry weight of the paper, at least a portion of said siliceous material being alkali metal silicate in an amount not exceeding about 2.5%, figured as SiO_2, by weight based on the dry weight of the paper.

6. The method of increasing the wet strength of paper while preserving the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish to the paper between 0.1% and about 2.5% sodium silicate, figured as SiO_2, by weight based on the dry weight of the paper, and heating said paper above 212° F. to deposit sodium silicate reducing the tendency of the paper fibres to swell upon the application of water, 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 the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish to the paper between 0.1% and about 2.5% sodium silicate, figured as SiO_2, 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 above 212° F. to deposit sodium silicate reducing the tendency of the paper fibres to swell upon the application of water, 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 the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish to the paper between 0.1% and about 8% siliceous material, figured as SiO_2, by weight based on the dry weight of the paper, neutralizing a portion of the sodium silicate absorbed by the paper to convert it into silicic acid and to provide between 0.1% and about 2.5% sodium silicate, figured as SiO_2, by weight based on the dry weight of the paper, and heating said paper above 212° F. to deposit sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper.

9. The method of increasing the wet strength of paper while preserving the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish to the paper between 0.1% and about 8% siliceous material, figured as SiO_2, by weight based on the dry weight of the paper, neutralizing a portion of the sodium silicate absorbed by the paper to convert it into silicic acid and to provide between 0.1% and about 2.5% sodium silicate, figured as SiO_2, by weight based on the dry weight of the paper, said 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 above 212° F. to dry it and to deposit sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper.

10. The method of increasing the wet strength of paper while preserving the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish between 0.1% and about 8% siliceous material, figured as SiO_2, by weight based on the dry weight of the paper and with a solution of an ammonium salt in an amount to convert a sufficient portion of said sodium silicate into silica upon heating to provide between 0.1% and about 2.5% sodium silicate, figured as SiO_2, by weight based on the dry weight of the paper, and heating said paper above 212° F. to cause said conversion and to deposit sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper.

11. The method of increasing the wet strength of paper while preserving the dry tear resistance thereof, which comprises impregnating paper with a solution of sodium silicate in an amount sufficient to furnish between 0.1% and about 8% siliceous material, figured as SiO_2, by weight based on the dry weight of the paper and with a solution of an ammonium salt in amount to convert a sufficient portion of said sodium silicate into silica upon heating to provide between 0.1% and about 2.5% sodium silicate, figured as SiO_2, by weight based on the dry weight of the paper, said impregnation being conducted at a point in the production of said paper after the formation of an interfelted web and prior to completion of the drying thereof, and heating said paper above 212° F. to dry it and to cause said conversion to deposit sodium silicate and silica reducing the tendency of the paper fibres to swell upon the application of water, within and upon the surface of the fibres throughout the interfelted structure of the paper.

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