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[54] **METHOD FOR SURFACE SIZING OF PAPER**
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ABSTRACT: Paper or a paper product which has been internally sized prior to web formation by incorporation in the pulp slurry of a fatty acid sizing agent, such as the sodium salt of stearic acid, and precipitation of the sizing agent onto the pulp fibers with a water-soluble polyvalent metal salt, such as alum or aluminum chloride, is surface sized after web formation with an aqueous solution containing an aldonic acid such as gluconic acid or a water-soluble salt of an aldonic acid such as sodium gluconate.

METHOD FOR SURFACE SIZING OF PAPER

This invention relates in general to the manufacture of paper and paper products, such as paperboard. More particularly, this invention relates to a method for surface sizing subsequent to web formation of paper which has been internally sized prior to web formation, to novel sizing compositions utilized in practicing this method, and to the sized paper or paper product produced therewith.

Sizing of paper is a very old and well-established art and a wide variety of materials have been proposed heretofore for this purpose. As is well known, the sizing agent may be applied to the fibers during the papermaking operation, in which case the process is called internal sizing (also known as beater sizing or engine sizing), or it may be applied to the surface of the paper after web formation, in which case it is called external or surface sizing. A particularly important class of sizing agents for internal sizing are the fatty acid sizing agents, i.e. sodium, potassium or ammonium salts of long-chain saturated fatty acids. In employing these agents, it is conventional practice to add the sizing agent to the paper furnish and thereafter add a precipitating agent which aids in setting the size of the papermaking fibers. The precipitating agents used are water-soluble polyvalent metal salts, such as alum or aluminum chloride. Use of the aforesaid combination of sizing agent and precipitating agent can be accomplished in conventional papermaking machines without the aid of any special apparatus. Moreover, the materials used are of low cost and are generally quite effective in imparting to paper the ability to resist penetration by liquids. However, there are certain significant limitations and disadvantages associated with their use. For example, in some instances the water resistance attainable with these agents is inadequate. Furthermore, in using these sizing agents at the concentrations customarily employed serious problems can arise with regard to formation of translucent "spots" in the paper and there may also be problems associated with accumulation of the sizing agent at the press rolls of the papermaking machine or with clogging of pipes or other equipment by the sizing agent.

An improved method of internal sizing of paper and paper products utilizing a fatty acid sizing agent and a precipitating agent is disclosed and claimed in copending U.S. patent application Ser. No. 800,742, entitled "Improved Method For Sizing Paper," filed by Oliver J. Schulwitz and L. E. Herdle on Feb. 19, 1969, and assigned to the same assignee as the present application. As disclosed in the aforesaid copending application Ser. No. 800,742, a water-soluble polyfunctional carboxylic acid salt is incorporated in the pulp slurry in addition to the fatty acid sizing agent and the precipitating agent, with the result that the paper or paper product exhibits improved resistance to penetration by water or aqueous solutions.

It has now been discovered that paper or paper products which have been internally sized by application of a fatty acid sizing agent followed by a precipitating agent can be subjected to surface sizing, i.e., treated with a sizing solution after web formation, to provide increased resistance to penetration by water or aqueous solutions. Thus, while the method of the aforesaid copending application Ser. No. 800,742 is directed to a modified internal sizing process which represents an improvement in the conventional process of internal sizing with a fatty acid sizing agent and a precipitating agent, the present invention is directed to a surface sizing method for use with paper which has already been internally sized with a fatty acid sizing agent and a precipitating agent in accordance with conventional practice.

More specifically, the method of this comprises the step of surface sizing paper or paper products, which have been internally sized during their manufacture with a fatty acid sizing agent and a water-soluble polyvalent metal salt precipitating agent, by application thereto of a solution of an aldonic acid or a water-soluble salt of an aldonic acid. The aldonic acid, or water-soluble salt thereof, may be utilized by itself or as an additive in conventional sizing solutions heretofore used for sur-

face sizing of paper and will provide a substantial increase in resistance to penetration by water or aqueous solutions, including alkaline, neutral and acidic solutions. Surface sizing, or as it is frequently termed, "tub sizing," is ordinarily effected in an "in-line" operation as one step of the paper manufacturing process, and this is the usual and preferred manner in which the surface sizing method of this invention is employed. However, it is also feasible to utilize the surface sizing method of this invention to treat paper which has been dried, wound into rolls, and kept in storage and/or shipped from the paper mill to the customer, so long as it is paper that has been internally sized during its manufacture by the use of a fatty acid sizing agent and a precipitating agent.

For the purposes of this invention, the paper or paper product can be made from any conventional type of pulp, such as sulfite, kraft or soda, cooked softwood, hardwood or groundwood, rag, rope, jute, and the like, and the pulp can be either bleached or unbleached. Partially esterified cellulose fibers, such as are described in U.S. Pats. No. 3,062,679 and 3,096,231, can be used and the furnish may, if desired, include minor amounts of synthetic organic fibers and/or mineral fibers.

The fatty acid sizing agents utilized in practicing this invention are well known in the papermaking art. They are used in place of the more commonly utilized rosin size where it is necessary that the paper resist penetration by organic solvents as well as penetration by aqueous solutions, an important example of such use being the manufacture of photographic papers. The fatty acid sizing agents known to the art are sodium, potassium or ammonium salts of saturated fatty acids of 12 to 22 carbon atoms, such as lauric acid, tridecyl acid, myristic acid, pentadecyl acid, palmitic acid, margaric acid, stearic acid, nondecyl acid, arachidic acid, behenic acid, and the like. For the purposes of this invention, the preferred fatty acids are those containing 16 to 18 carbon atoms and it is particularly preferred to employ a salt of stearic acid, especially sodium stearate, as the sizing agent. The fatty acid salt used as the size may be prepared from a single saturated fatty acid, or from a mixture of two or more of such acids, and unsaturated fatty acids may be present in the mixture in minor proportions.

In order to set the fatty acid sizing agent, it is conventional practice in the papermaking art to utilize a water-soluble polyvalent metal salt which reacts with the sizing agent to precipitate it onto the papermaking fibers, apparently in the form of an insoluble complex. Suitable salts for this purpose are those in which the polyvalent metal ion is the aluminum, iron or chromium ion and the anion moiety is derived from a strong mineral acid, for example, the sulfate, nitrate, or chloride ion. Illustrative examples of such salts are aluminum chloride, aluminum sulfate, aluminum nitrate, ferric sulfate and chromic sulfate. It is preferred to employ aluminum salts in the practice of this invention. Aluminum sulfate and potassium sulfate-aluminum sulfate salts are ordinarily referred to as alums; the term "anhydrous alum" referring to $\text{Al}_2(\text{SO}_4)_3$, the term "papermakers alum" referring to $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and the term "common alum" referring to $\text{KA}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. For the purposes of this invention, preferred precipitating agents are aluminum chloride (AlCl_3) and papermakers alum.

For further details of the process of internal sizing of paper with a fatty acid sizing agent and a water-soluble polyvalent metal salt precipitating agent, reference may be made to U.S. Pat. Nos. 1,840,399 and 3,096,231.

In accordance with this invention, paper or a paper product which has been internally sized with a fatty acid sizing agent and a water-soluble polyvalent metal salt precipitating agent is surface sized, i.e., sized after web formation, by contacting it with a solution comprising an aldonic acid or a water-soluble salt of an aldonic acid. The aldonic acids are acids of aldoses, e.g., acids of aldopentoses, aldohexoses, aldohexoses, and so forth, and are commonly referred to as sugar acids. Illustrative examples of aldonic acids are arabonic acid, xylonic acid, ribonic acid, gluconic acid, talonic acid, galactonic acid,

idonic acid, gulonic acid, mannonic acid, altronic acid, allonic acid, glucoheptonic acid, mannootonic acid, mannononic acid, and the like. Illustrative examples of the water-soluble salts that can be employed include the ammonium salt, alkali metal salts such as the sodium or potassium salts, and alkaline earth metal salts such as the calcium, barium and magnesium salts. Mixtures of two or more of the aforesaid aldonic acids or aldonic acid salts can be employed, is desired. For purposes of convenience in describing this invention, the term "aldonic compound" will be employed hereinafter to mean one or more aldonic acids or water-soluble aldonic acid salts and the term "aldonic solution" will be employed to mean an aqueous solution containing one or more aldonic acids or water-soluble aldonic acid salts.

In effecting internal sizing of paper which is to be surface sized by the method of this invention, the fatty acid sizing agent and water-soluble polyvalent metal salt precipitating agent can be utilized within a broad range of proportions. Thus, the fatty acid sizing agent may be advantageously employed in a proportion of from about 0.001 to about 0.1 parts of fatty acid salt per part by weight of the papermaking fibers on a dry basis, with the preferred proportion being in the range from about 0.005 to about 0.02 parts per part by weight. Within these agents ranges the specific amount used will, of course, depend on such factors as the type of pulp employed, the operating conditions of the papermaking process, and the particular end use for which the paper or paper product is intended. The amount of precipitating agent used will typically be in the range from about 0.2 to about 10 parts per part by weight of sizing agent, i.e., about 0.2 to about 10 parts of polyvalent metal salt per part by weight of fatty acid salt, and preferably in the range from about 0.5 to about 2 parts per part by weight. The consistency of the pulp slurry at the time these agents are added can vary widely, for example, amounts of from about 0.1 percent to about 5 percent of dry fibers based on the total weight of the slurry are ordinarily suitable.

The aldonic compound can be utilized in any penetration resistance improving amount in accordance with this invention. Typical amounts of the aldonic compound range from about 0.005 to about 1 part per part by weight of the fatty acid sizing agent which has been incorporated in the paper, i.e., about 0.005 to about 1 part of aldonic compound per part by weight of fatty acid salt, with the preferred amount being in the range of from about 0.01 to about 0.1 part per part by weight.

Any suitable method of contacting the paper with the aldonic solution can be utilized in the practice of this invention. For example, the paper web can be dipped in the solution, or the solution can be sprayed, onto the web, or the web can be passed between padded rollers which soak up the solution and apply it to the web. It is not essential that the paper be dried to a low water content before contacting it with the aldonic solution, but it is preferred that it be relatively dry, e.g., a water content of 10 percent or less, so that it will take up an adequate amount of the solution. If the paper web is wet when it is immersed in the solution there will still be a certain amount of aldonic compound taken up by the paper as a result of diffusion, but this may not be adequate in some instances to achieve the full benefits of the invention.

To effectively control the amount of aldonic compound incorporated in the paper, the web can be immersed in the aldonic solution and then passed through squeeze rolls to remove excess solution. In employing this procedure, the concentration of aldonic compound in the solution can vary over a wide range, as desired. Thus, the aldonic solution which is used can be a very dilute solution, e.g., a concentration of as little as about 0.1 percent by weight of aldonic compound, or a relatively concentrated solution containing any amount of aldonic compound up to the maximum amount which can be dissolved in water at the solution temperature employed. Depending on the duration of immersion in the solution and the amount of pressure to which the paper is subjected in the squeeze rolls, a wet pickup of up to about 30 percent is readily

achieved, i.e., the web is impregnated with up to about 30 percent of its own weight of aldonic solution. Use of a solution with a relatively high concentration of aldonic compound permits the use of a relatively low wet pickup with the resulting advantage that only a small amount of water then needs to be removed in the subsequent drying of the paper web.

Surface sizing of paper with the aldonic solution can be carried out at room temperature or at elevated temperatures, as desired. Since it is difficult for the aldonic solution to effectively penetrate the paper, because the paper has already been internally sized, it is advantageous to heat the aldonic solution, it having been found that a hot solution is better able to penetrate into the paper. Although any temperature from room temperature up to the boiling point of the solution can be satisfactorily employed, optimum results are obtained with a solution which is at or near its boiling point. By use of a hot solution, substantially higher wet pickup can be achieved than is the case with solutions at room temperature. Thus, for example, with a solution temperature of 100° C. the wet pickup may be as high as about 90 percent. In production use, a satisfactory temperature may be conveniently provided by introducing the hot paper sheet from the dryer directly into a warm solution.

In view of the difficulty of getting the surface size solution to penetrate the paper, the method of this invention is most effective when employed with lightweight paper, e.g. a basis weight of less than about 20 pounds/1,000 ft.². For heavy paper, and paper products such as paperboard, the internal sizing procedure disclosed in applicants' hereinbefore described copending U.S. Pat. application Ser. No. 800,742 is preferred.

Following application of the aldonic solution in accordance with this invention, the paper web is dried to remove the water. While drying can be accomplished by simply allowing the paper to remain at room temperature for a sufficient period of time, the usual and preferred practice is to dry the paper at an elevated temperature. Temperatures and drying times customarily utilized in the drying step which follows tub sizing in conventional papermill practice are suitable in carrying out the method of this invention. Typical drying conditions are a temperature of from about 75° C. to about 125° C. for a period of from about 15 seconds to about 2 minutes, the higher temperatures usually being employed in conjunction with the shorter times. Drying the paper by contacting the web with the a heated drum having a surface temperature of about 100° C. is a particularly effective procedure.

While the essential feature of the present invention is the treatment after web formation with an aldonic solution of paper which has been internally sized with a fatty acid sizing agent and a precipitating agent, as hereinbefore described, other additives commonly used in the papermaking art can also be utilized to advantage in manufacture of the improved paper and paper products of this invention. Thus, for example, it may be desired in particular instances to employ such additives as fillers, e.g., clays or pigments such as titanium dioxide, wet strength resins, e.g., the amino-aldehyde or polyamide-epichlorohydrin resins, dry strength agents, e.g., starches, including both ordinary starch and cationic starch, or polyacrylamide resins, and water-soluble gum, e.g., cellulose ethers such as carboxymethyl cellulose.

In carrying out surface sizing of paper in accordance with this invention, the aldonic compound may be used by itself, i.e., the sizing solution may be a solution of an aldonic compound free of any additional ingredients, or the aldonic compound may be added to conventional tub sizes heretofore used for sizing of paper. A substantial improvement in the water resistance of the paper, as well as its resistance to penetration by acidic or alkaline solutions, will be achieved in either instance. The tub size in which the aldonic compound is incorporated may have a neutral, alkaline or acidic pH. Illustrative examples of conventional tub sizes to which an aldonic compound may be added are dilute solutions of gelatin or starch, e.g., an aqueous solution containing 2 to 6 percent by weight of

gelatin plus a trace of a microbicide or an aqueous solution containing 2.5 to 7 percent by weight of an oxidized starch or a chlorinated starch plus a trace of a microbicide. Sufficient aldonic compound should be added to the tub sizing solution to provide for incorporation in the treated paper of an amount of aldonic compound sufficient to effect an improvement in the penetration resistance of the paper. Preferred amounts for this purpose have been described hereinbefore.

The paper and paper products of this invention may be utilized to advantage wherever good resistance to penetration by aqueous solutions is needed. Thus, the invention may be utilized in manufacture of wrapping paper, in manufacture of paper to be used for preparation of gummed labels, in manufacture of paper employed to make bags, and in manufacture of paperboard for use as making boxes. An especially important use of the method disclosed herein is its use in the manufacture of photographic papers, in view of the fact that such papers should be highly resistant to penetration by aqueous solutions encountered in photographic processing operations, including both strongly acid and strongly alkaline solutions. For the manufacture of such photographic papers, optimum results are achieved in accordance with this invention by the use of sodium stearate and aluminum chloride in the internal sizing and an aqueous solution of sodium gluconate as the surface sizing solution, and this combination represents a preferred embodiment of the invention.

The invention is further illustrated by the following examples of its practice. In these examples, amounts of additives based on fiber content of the pulp slurry are in terms of weight percent of the additive based on the bone-dry fiber weight. The sodium stearate sizing agent was prepared from commercial stearic acid, which is a mixture of stearic and palmitic acids also containing minor amounts of other saturated fatty acids.

EXAMPLE 1

Paper with a basis weight of 41 pounds/1,000 ft.² was formed on a conventional Fourdrinier paper machine from northeastern softwood sulfite pulp. In preparing the paper there was added to the pulp slurry 0.3 percent of a melamine-formaldehyde wet strength agent, 1.2 percent of sodium stearate, 2.7 percent of starch, and sufficient aluminum chloride to reduce the pH of the pulp slurry to 4.5 (this required 0.84 parts of aluminum chloride per part by weight of sodium stearate). A portion of the paper, taken from the drying end of the papermaking machine prior to any tub sizing, was dipped in an aqueous solution containing 4 weight percent gelatin, passed between press rolls to remove excess liquid, and dried against a heated drum at 110° C. A second portion of the paper was treated in an identical manner except that the solution in which it was dipped contained 4 weight percent gelatin and 0.25 weight percent sodium gluconate. To determine the penetration resistance, samples of each of these two papers were subjected to an acid penetration test in which the paper is contacted on both sides with an aqueous solution containing 7.5 grams of sodium chloride and 625 cc. of glacial acetic acid per liter of solution and the time in seconds until the paper will conduct an electric current of 20 milliamperes is measured. The value obtained for the paper dipped in the solution of gelatin was 165, while the value obtained for the paper dipped in the solution of gelatin and sodium gluconate was 193.

EXAMPLE 2

Paper with a basis weight of 18 pounds/1,000 ft.² was formed on a conventional Fourdrinier paper machine from a mixture of 88 percent northeastern softwood sulfite pulp and 12 percent bleached kraft pulp. In preparing the paper there was added to the pulp slurry 1.5 percent of the cationic thermosetting polyamide-epichlorohydrin wet strength resin prepared from diethylene triamine, adipic acid and epichlorohydrin, 2.0 percent of sodium stearate, 0.5 percent

of carboxymethyl cellulose, and sufficient aluminum chloride to reduce the pH of the pulp slurry to 4.5. Portions of the paper were surface sized in the same manner as in example 1 using in one case a 4 weight percent gelatin solution and in the other case a solution containing 4 weight percent gelatin and 0.25 weight percent sodium gluconate. To determine the penetration resistance, samples of each of the two papers were subjected to the acid penetration test described in example 1 and also to a carbonate penetration test. In the carbonate penetration test, the paper is contacted on both sides with a 5 percent aqueous solution of sodium carbonate and the time in seconds until the paper will conduct an electric current of 50 milliamperes is measured. The values obtained of the paper dipped in the solution of gelatin were an acid penetration of 10 seconds and a carbonate penetration of 86 seconds, while the values obtained for the paper dipped in the solution of gelatin and sodium gluconate were an acid penetration of 96 seconds and a carbonate penetration of 126 seconds.

EXAMPLE 3

A sample of the paper whose preparation is described in example 2 above was taken from the papermaking machine, dipped in water, passed between press rolls to remove excess water, and dried against a heated drum at 110° C. A second sample of the same paper was dipped in a 0.25 weight percent solution of sodium gluconate in water, passed between press rolls to remove excess solution and dried against a heated drum at 110° C. The dipped in water had an acid penetration resistance of 9 seconds and a carbonate penetration resistance of 55 seconds, while the paper dipped in the sodium gluconate solution had an acid penetration resistance of 54 seconds and a carbonate penetration resistance of 132 seconds.

EXAMPLE 4

A sample of the paper whose preparation is described in examples 2 above, designated hereinafter as sample A, was dipped into water at 50° C. for 30 seconds. A second sample of the same paper, designated as sample B, was dipped into 0.1 percent by weight sodium gluconate solution at 50° C. for 30 seconds and a third sample of the same paper, designated as sample C, was dipped into 0.1 percent by weight sodium gluconate solution at 100° C. for 30 seconds. After pressing the paper to remove excess liquid, samples A and B had a wet pickup of 45 percent and sample C a wet pickup of 89 percent. Each sample was dried and the penetration resistance determined. The acid penetration values for samples A, B and C were 58, 299 and 559 seconds, respectively, while the carbonate penetration values were 98, 168 and 167 seconds, respectively.

EXAMPLE 5

Six samples of the paper whose preparation is described in example 2 were dipped in 0.1 percent by weight sodium gluconate solution under varying conditions of solution temperature and immersion time and, after drying, acid penetration values were determined for each of the samples. Results obtained were as follows:

Sample No.	Immersion Time (seconds)	Temperature (° C.)	Acid Penetration Value (seconds)
1	5	27.5	140
2	30	27.5	230
3	5	50	225
4	30	50	300
5	5	100	470
6	30	100	560

Increasing the time during which the paper was immersed in the solution beyond 30 seconds did not provide any further improvement in penetration resistance.

EXAMPLE 6

Paper with a basis weight of 24 pounds/1,000 ft.² was formed on a conventional Fourdrinier paper machine from a mixture of northeastern and western softwood sulfite pulps. In preparing the paper there was added to the pulp slurry 1.2 percent of sodium stearate and sufficient aluminum chloride to reduce the pH of the pulp slurry to 4.5. A sample of the paper was dipped in water for 5 seconds, drained, and dried for 5 minutes in an oven at 110° C., and a second sample was dipped for 5 seconds in a 0.1 weight percent solution of sodium gluconate in water and similarly drained and dried. The penetration resistance of each sample of paper was determined by an acid absorption test in which there was measured the time in seconds required for a drop of a 62.5 weight percent solution of acetic acid in water to be absorbed, the drop being of the exact same size in each instance. The paper dipped in water had an acid absorption value of 553 seconds while the paper dipped in the sodium gluconate solution had an acid absorption value of 712 seconds.

EXAMPLE 7

A sample of the paper whose penetration is described in example 6 above was dipped in boiling water for 5 seconds, drained, and dried for 5 minutes in an oven at 110° C. A second sample of the same paper was dipped for 5 seconds in a boiling solution of 0.1 weight percent sodium gluconate in water and similarly drained and dried. The paper dipped in boiling water had an acid absorption value of 190 seconds while the paper dipped in the boiling sodium gluconate solution had an acid absorption value of 1,050 seconds.

As illustrated by the above examples, surface sizing with an aldonic solution, such as sodium gluconate solution, of paper which has been internally sized with a fatty acid sizing agent, such as sodium stearate, and a precipitating agent, such as aluminum chloride, brings about a very substantial improvement in the penetration resistance of the paper. The method of this invention can be used to provide greater penetration resistance than is obtainable solely by internal sizing with a fatty acid sizing agent and a precipitating agent or it can be used to reduce the amount of fatty acid sizing agent employed while still providing the same level of penetration resistance as would be obtained with the larger amount of fatty acid sizing agent. Thus, by this means, significant economic savings resulting from the reduced use of fatty acid sizing agent can be achieved and many of the problems heretofore encountered as a result of the relatively large amounts of fatty acid sizing agent needed can be eliminated, or at least substantially reduced.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A method for surface sizing of paper or paper products which have been internally sized with a fatty acid sizing agent and a water-soluble polyvalent metal salt precipitating agent, comprising the step of incorporating into said paper or paper product subsequent to web formation a penetration resistance improving amount of an aldonic acid or a water-soluble salt thereof by contacting said paper or paper product with an aqueous solution consisting essentially of said aldonic acid water-soluble salt thereof.

2. A method for surface sizing of paper or paper products which have been internally sized with a fatty acid sizing agent and a water-soluble polyvalent metal salt precipitating agent, comprising the step of incorporating into said paper or paper

product subsequent to web formation a penetration resistance improving amount of gluconic acid or a water-soluble salt thereof by contacting said paper or paper product with an aqueous solution consisting essentially of said aldonic acid or water-soluble salt thereof.

3. A method for surface sizing of paper or paper products which have been internally sized with sodium stearate and aluminum chloride, comprising the step of incorporating into said paper or paper product subsequent to web formation a penetration resistance improving amount of sodium gluconate by contacting said paper or paper product with an aqueous solution consisting essentially of said sodium gluconate; the amount of said sodium gluconate in said aqueous solution being at least about 0.1 weight percent.

4. The method as described in claim 1 wherein said fatty acid sizing agent is a salt of a saturated fatty acid of 16 to 18 carbon atoms.

5. The method as described in claim 1 wherein said fatty acid sizing agent is a salt of stearic acid.

6. The method as described in claim 1 wherein said fatty acid sizing agent is sodium stearate.

7. The method as described in claim 1 wherein said precipitating agent is an aluminum salt.

8. The method as described in claim 1 wherein said precipitating agent is aluminum chloride.

9. The method as described in claim 1 wherein said aqueous solution is a solution of sodium gluconate.

10. The method as described in claim 1 wherein said aqueous solution is a solution of gelatin and sodium gluconate.

11. The method as described in claim 1 wherein said paper is dipped in said aqueous solution and then passed between rolls to remove excess solution therefrom.

12. The method as described in claim 1 wherein said aqueous solution is at an elevated temperature when brought into contact with said paper or paper product.

13. The method as described in claim 1 wherein said aqueous solution is essentially at its boiling point when brought into contact with said paper or paper product.

14. The method as described in claim 1 additionally comprising the step of drying said paper or paper product at a temperature of from about 75° C. to about 125° C. after contact with said aqueous solution is effected.

15. In a method for the manufacture of paper or a paper product in which internal sizing to render the paper or paper product resistant to penetration by aqueous solutions is effected by incorporating in the pulp slurry prior to web formation a fatty acid sizing agent and precipitating said agent onto the pulp fibers by the addition of a water-soluble polyvalent metal salt, the improvement comprising subjecting said paper or paper product subsequent to web formation to surface sizing with an aqueous solution consisting essentially of an aldonic acid or water-soluble salt thereof, whereby the ability of the paper or paper product to resist penetration by aqueous solutions is enhanced.

16. The method as described in claim 15 wherein said fatty acid sizing agent is sodium stearate, said polyvalent metal salt is aluminum chloride, and said aldonic acid is gluconic acid.

17. The method as described in claim 15 wherein said surface sizing is effected with an aqueous solution containing at least 0.1 weight percent of sodium gluconate.

18. Paper or paper product surface sized by the method of claim 1.

19. Paper or paper product surface sized by the method of claim 2.

20. Paper or a paper product surface sized by the method of claim 3.

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