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(54) Method of sizing paper.

(57) A starch which has been reacted with a dicarboxylic acid anhydride such as octenyl succinic anhydride is applied to a formed paper web from the size press. The starch combines with a multivalent metal ion e.g. (aluminium) already present in the paper web to become hydrophobic, and thereby impart a high level of water resistance concentrated at the surface of the paper.

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Method of Sizing Paper.

This invention relates to a method of sizing paper.

Conventional high-grade, water-resistant papers are made by adding rosin(a natural product from pine trees) at the wet-end of the papermaking process. The rosin is barely water-dispersible, and in the presence of alum, it precipitates in the fibre web as the paper sheet is being formed. Variations in the composition of the paper-making furnish can have an adverse effect on the amount of rosin which precipitates on the papermaking wire. The usual commercial practice to compensate for such variations is to add an excess amount of rosin to the furnish to ensure sufficient pickup to make a paper having the desired level of water-resistance.

There are increasing numbers of paper mills which use recycled paper as part of the raw material in the wet-end furnish of the papermaking process. As material economy measures are required, and conditions of pH, surface charge and pulp constituents in the papermaking machine are changed, the materials which can be used to impart water-resistance to the paper must meet new requirements without sacrificing paper quality.

In some earlier attempts to make a water-resistant paper by adding rosin/alum compounds at the size press, too much rosin/ alum was employed and the excess tended to coagulate and gum up the size press, causing the resulting paper to be "spotty". An improved method for applying rosin/alum at the size press is disclosed in United States Patent Application Serial Number 909,854 filed May 26 1978. The method described in that application, however, employs rosin and therefore, is limited in its possible uses by the availability of rosin and its compatibility with the other components of the paper. The method also requires that alum be added at the size press along with the rosin. This is in addition to the alum normally included in the furnish at the wet-end of the papermaking machine. To applicants' knowledge, there has not yet been a successful commercial method of obtaining water-resistant paper by means of sizing with a starch derivative at the size press in a papermaking process.

United States Patent 3,279,975 describes a method of surface sizing using the reaction product of an unsaturated acid and petroleum resin. Various other materials are disclosed in the literature for use as sizing agents for the surface treatment of paper. Such materials include emulsions of the reaction product of an unsaturated dibasic acid or anhydride of the acid with, for example, a maleated petroleum resin, alkyl ketene dimers, alkali-soluble styrene copolymers, chromium complexes of fluorocarbon chemicals, and others. Such materials have not attained widespread use because of costs, or control problems, such as the "gum up" phenomena, or drying problems.

United States Patents, 2,613,206; 2,461,139 and 3,091,567 disclose certain hydrophobic starch acid-esters and various uses for these starch derivatives. A method of making these starch acid-esters and their combination with multivalent metal ions such as aluminium is disclosed in United States Patent 2,613,206, and the hydrophobic character of the starch is set forth. However, the industrial uses suggested for the resulting starch derivative do not include paper sizing. The mentioned uses include: anti-offset spray for preventing ink transfer between freshly printed sheets; insecticide carriers, delustering agent in the manufacture of cellulose acetate rayons, delustering agent in lacquer-type paints and coatings; rubber finishing agent; and textile sizing and finishing agent. This patent makes no mention of any use of the subject starch derivative in paper sizing, or of thinning it prior to use. Paper sizing and coating is mentioned in U.S. Patent 2,661,349, Col. 11, lines 5-10, but on ly in a general way. There are no examples illustrating such uses.

United States Patent 2,461,139 describes a method of making starch ester derivatives by reacting starch, in the presence of moisture, with organic acid anhydrides to obtain an inhibited starch having a reduced tendency to gel. The patent states that an alkaline reaction medium (pH 7-11) is essential to the practice of the inventive method. "An amazing increase in water absorptive powers" is shown by starch treated with succinic anhydride. Papermaking is mentioned (Column 3, lines 31-34), but the starch derivative is only described as a replacement for tuber starches in papermaking for its non-gelling nature and its superior cohesiveness. Apparently, the application under consideration was that of a binder in the wet-end, or furnish, of the paper machine. Examples 4 and 5 of the subject patent describe making a so-called "thin-boiling" starch, but only with maleic and acetic anhydride. Example 6 describes thinning a starch maleate ester to obtain a thin-boiling starch. Both Example 8 and 9 describe reacting starch with succinic anhydride, and the general disclosure states that the starch derivatives of any of the examples may be further converted, as by acid hydrolysis, for example. There is no mention of sizing paper, however, and the starch derivative obtained using succinic anhydride is described as a "high water absorptive starch" (column 12, lines 2 and 3 of U.S. Patent 2,461,139).

United States Patent 3,091,567 is directed to a starch acid-ester encapsulating agent having controlled water repellency obtained by reacting the starch acid-ester with a compound containing a polyvalent metallic ion. The starch acid-ester may be obtained from the reaction of starch with octenyl succinic acid anhydride.

General language in this patent suggests that the starch used to make the described starch acid-ester "may have been previously modified ...by hydrolysis, oxidation ..." etc. (Column 3, lines 22-24). This patent, however, discloses only one use of the starch derivative. It is used to encapsulate water-insoluble substances to permit slow, gradual release of the encapsulated material. There is no mention of possible use in a papermaking process.

Recently published Japanese Patent Specification 53-61706 describes sizing of paper or cardboard with a sizing composition comprising 1-20 parts of hydrophobic starch and 99-80 parts of non-hydrophobic starch. The hydrophobic starch consists of a dicarboxylic acid starch monoester in which the carboxylic acid groups are on adjacent carbon atoms. The dicarboxylic acid may have 8-22 carbon atoms, and may have alkyl or halogen substituent groups. Included in Example 2 of the subject Japanese Specification is 1-octenylsuccinic anhydride as an esterification agent for making Starch "C". The method of Example 1 was followed to make Starch "C", and the level of substitution was reported to be 0.027 d.s.

A starch derivative like the above Starch "C" was used to size a paper web made from bleached kraft pulp containing about 1% alum, based on the pulp dry weight. The dispersed sizing composition contained 5% of a hydrophobic starch (like Starch "C", but with a d.s. of 0.032), and 95% of a non-hydrophobic cationic starch (having about 0.24% by wt. nitrogen content). The dispersion had a solids level of about 4-5%. Sixty pounds of the size dispersion per ton of paper was applied. Rosin was also used in the sample runs(at 12 and 6 kg/metric tonne respectively).

The above derivatized starch sizing agent and sizing method differs from the subject sizing composition and method in at least the following important ways:

Japanese Patent Specification 53-61706	Subject Application
Highly substituted starch derivative about 0.03 d.s. of octenyl succinic acid ester groups.	About 0.01 d.s. of ester groups preferred. Upper limit about 0.023.
Apparently no thinning prior to use in size press - intended for blending with conventional size press starch, such as a cationic size press starch.	Always thinned prior to use in size press. Intended for use as the sole size press starch.
When bulk handling system is used, a dual bulk handling system at the paper mill is required for two kinds of starch if on-site blending is to be done, or manual handling will be required.	Only a single bulk handling system required for one size press starch.
Results obtained in Example 4 do not show any significant improvement over what could be expected with 12 kg of rosin per metric tonne of paper. This amount of rosin can be expected to give the results reported without any addition of the hydrophobic starch derivative. 6 and 12 kg rosin/tonne of paper were used, which is about six times as much rosin as used in the method of the subject invention.	Only the low substituted starch need be used with about 1-2 kg rosin/metric tonne of paper to control pick-up. With the above, 40-50 sec. Hercules is obtained in paper sized by the method of the subject invention.

It is not clear from the disclosure of the subject Japanese Specification that some alum must be present in the paper web as it enters the size press. In addition, it is believed that the overall expenses and materials cost to practice the method of the subject Japanese patent specification would be too high for use as a competitive method of sizing paper. The purpose of the present invention is to cut down on the excessive use of rosin. The method described in the Japanese patent specification does not substantially reduce the amount of rosin used, and it is believed that the same sizing effect is obtainable using the stated amounts of rosin without the highly substituted octenyl succinic acid starch ester. The results of the present invention are much superior to the results reported in the subject Japanese specification, and applicants use a starch derivative having a much lower level of substitution with only enough rosin present to control pick-up (1-2 kg rosin/tonne of paper).

The present invention provides a method of externally sizing a cellulosic web containing a multivalent metal ion to impart increased water resistance to the web by applying an aqueous sizing composition, to the cellulosic web, characterised in that the aqueous sizing composition contains from 2 to 15% by weight of a dicarboxylic acid starch ester obtained by reacting starch with a dicarboxylic acid anhydride having 8 to 22 carbon atoms which is an aliphatic, aromatic, alicyclic or bicyclic aliphatic dicarboxylic acid anhydride or substituted dicarboxylic acid anhydride, the said starch ester having a degree of substitution of the dicarboxylic acid anhydride in the range from 0.005 to 0.023 in that the aqueous sizing composition has a Brookfield viscosity in the range of 10 to 150 cps (No. 1 Spindle; 20 rpm; 66°C), in that the sizing composition has a pH of 4 to 7.5 and a temperature of 50 to 80°C and in that the sizing composition is applied to the cellulosic web at a rate of 10 to 100 kg per tonne. Preferably the starch ester is obtained by reacting starch with 1-octenyl succinic acid anhydride.

Thus the starch ester may be a 1-octenylsuccinic acid half ester of cornstarch, the degree of substitution of which is in the range of 0.008 to 0.016, e.g. a 1-octenylsuccinic acid half ester of cornstarch which is slightly oxidized so that the amount of protein remaining in said half ester is less than 0.1% by weight based on the weight of the starch.

Preferably the multivalent metal ion which may be aluminium, calcium, magnesium, manganese or barium is in the form of a slightly water-soluble salt, and is added to the aqueous furnish from which the cellulosic web is formed. Preferably the multivalent metal salt is aluminium and is obtained from aluminium chloride, aluminium sulphate or sodium aluminate. Thus the multivalent metal salt may be aluminium sulphate which is present in the cellulosic web in an amount of at least 5 kg aluminium sulphate per tonne of fibre in the cellulosic web, or sodium aluminate which is present in the cellulosic web in an amount of at least 1.5 kg per tonne of fibre in the cellulosic web.

Preferably the reduced viscosity of the starch ester is obtained by acid hydrolysis of the starch esterorby

thermal chemical treatment of the starch ester. Alternatively, the substituted starch may have been slightly oxidized, and the reduced viscosity obtained by high temperature thermal treatment, e.g. at 107 to 163°C. Preferably the paper web is free of rosin.

Thus the invention relates to a method of making a water resistant paper by sizing the paper web at the size press with anaqueous solution of a viscosity thinned, hydrophobic starch derivative. The preferred starch derivative is the starch acid-ester of octenyl succinic anhydride. Alum present in the web from the wet-end of the papermaking process reacts with the starch derivative to produce a water-resistant sheet. When this starch derivative is applied from a solution at the size press of the papermaking machine, it apparently combines with the alum in a unique way to produce a high level of water resistance concentrated at the surface of the paper. The multivalent metal ion (aluminium) is supplied from the sheet passing through the size press from the wet-end (furnish) of the papermaking machine, or if the wet-end composition does not contain alum, aluminium sulphate may be added to the furnish at the wet-end of the paper-making machine so that it is present in the web at the size press where the thin viscosity octenyl succinate starch acid-ester is applied.

The invention is illustrated by the following examples.

EXAMPLE 1

The starch acid-ester used in the method of the invention may be made as follows:

Pearl starch (100 parts, as is) is adjusted with water to a slurry of about 21-22° Bé (at 16°C). About 2.9 parts of 60° Bé sulfuric acid which has been diluted with 2.9 parts of water is then added to the above starch slurry, and the temperature is adjusted to 53°C.

The acid is allowed to convert the starch at 53°C for approximately five hours to reach a target alkali fluidity value of 56 ml., using a 10 g. sample of starch in 90 ml. of 0.375N NaOH for determining alkali fluidity value. When the target alkali fluidity has been reached, the pH of the thinned starch slurry is adjusted to 4.5-5.0 with 18° Bé soda ash (sodium carbonate). About 2.8 parts soda ash is required. The slurry is then screened, filtered, and the filter cake washed. The washed filter cake is then reslurried in water to 21-22° Bé(at 16°C) and the temperature is adjusted to 32-35°C. The slurry is then agitated vigorously throughout the remaining steps of the process.

Two parts of 1-octenyl succinic anhydride is then added to the slurry. Immediately thereafter, 5% NaOH solution is added to adjust the slurry pH to 6.5-7.5. The pH is maintained in this range (6.5-7.5) with 5% NaOH until the slurry pH remains constant. Approximately 2 ½ hours is required to reach pH equilibrium, with a total addition of about 0.5 parts NaOH.

The slurry is then adjusted to 6.0-6.5 pH with 30° Bé sulphuric acid (about 0.5 parts of 60° Bé H_2SO_4 required.) The reacted starch is then screened and filtered. The filter cake is thoroughly washed with water at 43°C maximum. The washed starch derivative is then dried and screened. The moisture content of the dried product should be in the range of 10-13%, and at least 1% by weight, dry solids basis, of 1-octenyl succinic anhydride should have been reacted with the starch. The above starch derivative is then ready to use in the method of the invention and its various embodiments described herein.

EXAMPLE 2

The starch derivative made according to the above Example 1 has been successfully used as a water resistant size press starch to impart a high degree of water resistance to paper when applied to a paper sheet during the papermaking process. The sheet should contain sufficient alum (sodium aluminate) from the wet-end of the Fourdrinier-type papermaking machine. The addition of this starch derivative at the size press also develops the internal strength properties as efficiently as any conventional size press starches.

A trial was conducted at a paper mill which normally includes alum (sodium aluminate) in the wet-end of the papermaking machine. This mill also normally used a fortified rosin in the wet-end and another starch (enzyme converted) at the size press to obtain borderline sizing. Various trial runs were made as described below. The tests indicated that a significant improvement in water resistance can be obtained through application of the subject starch derivative at the size press of a paper-making machine.

A number of runs were made on a commercial paper-making machine using the starch derivative of Example 1, added at the size press. A control run was made on the same papermaking machine using an enzyme converted pearl starch at the size press at the same solids level. Hercules H.S.T. #2 INK tests were performed, and the results recorded. In another series of tests, pearl starch and the starch derivative of Example 1 were applied at the size press. In both of the above cases, the starch solids at the size press was about 7.8%. The results of the subject test runs are reported below in Table I:

TABLE I

			HST #2 INK Second		
Percent Starch Solids	Sample Description	Percent Starch Pickup	Before Size Press	After Size Press	Remarks
7.8	Enzyme Converted Pearl Starch	4.56	39	90	Not nearly as much water resistance obtained, and 25% more internal size used.
7.8	Starch of Example 1	4.55	30	158	Internal size reduced 25%, but excellent water resistance obtained.

Table 1 shows that definite and effective sizing was obtained using the subject starch derivative, applied at the size press. Only borderline sizing was obtained when an enzyme converted pearl starch was used at the size press in combination with a fortified rosin in the wet-end. However, Table 1 shows that the subject starch derivative not only gave excellent water-resistant size effect to the paper, but the internal fortified rosin size was also reduced by 25%. In addition, the subject starch derivative had no adverse effect on other physical properties of the sheet, such as mullen, tear, wax, pick, opacity and brightness. The pH of the size press dispersion was maintained at about 6 during the tests. The level of alum in the newly formed sheet was about 7.5 to 10 kg per metric tonne expressed as alum. The amount of alum in the sheet was determined by the method set forth below following Example 3.

EXAMPLE 3

Another paper mill test was also conducted which further demonstrated the effectiveness of the subject starch derivative to produce a water-resistant sheet when the subject starch is applied at the size press of a paper machine as described below.

Table II below is a report of the second series of tests conducted at the same paper mill as Example 2 on the same commercial papermaking machine. The subject starch derivative was again applied at the size press in the various combinations described in Table II:

Table II

Percent Starch Solids	Sample Description	Percent Starch Pickup	HST #2 INK Seconds Before Size Press	HST #2 INK Seconds After Size Press	Remarks
7.5	50% Enzyme-Converted Pearl Starch 50% Starch of Example 1	3.1	17	149	Excellent water resistance from the Example 1 starch.
7.5	100% Enzyme-Converted Pearl Starch	3.0	17	61	Water resistance dropped markedly as compared to No. 1 when Example 1 starch omitted.
7.5	50% Enzyme-Converted Pearl Starch 50% Starch of Example 1	3.0	17	189	Water resistance again restored when Example 1 starch added back.

As seen in Table II, the percent starch solids at the size press was about 7.5%, the particular starches comprising the total starch solids were changed as noted from a 50/50 blend of the starch of Example 1 and an enzyme-converted pearl starch to 100% enzyme converted pearl starch and then back to a 50/50 blend of the above starch derivatives.

The effect on the H.S.T. #2 INK test results caused by removing the starch derivative of the subject invention from the size press starch blend was dramatic and clear. Excellent water resistance (149 sec.) was obtained when a 50/50 blend was used which included the starch derivative of the subject invention. The H.S.T. #2 INK test fell in value by a factor greater than two to a value less than one-half the initial value (61 sec.). When the 50/50 blend of enzyme converted pearl starch and the starch derivative of Example 1 herein was again restored in the size press, the H.S.T. #2 INK test more than tripled in value when compared to 100% enzyme-converted pearl starch applied at the size press. This example clearly establishes that the increased sizing is attributable to the starch derivative of Example 1 and not to some other cause. the percent starch pick-up was also measured in this trial and was about 3%. The test shows that a 50/50 blend of an enzyme converted pearl starch with the subject starch derivative of Example 1 proved very adequate to obtain excellent water resistance when applied at the size press.

Apparently, the level of octenyl succinate groups on the paper web in the range of substitution described is what determines the level of water resistance in the resulting paper, not the amount of starch used, although the starch *per se* does contribute internal strength to the paper web. In other words, a starch derivative having a d.s. of 0.016 can be used in a smaller quantity to obtain the same level of water resistance obtainable from a larger quantity of a starch derivative having a lower level of octenyl succinate groups therein. When the substitution level of octenyl succinate groups is 0.016 or lower, it appears to be unnecessary to add any other starch, because enough of the subject starch is then present to provide both water resistance and internal strength to the paper. The lower d.s. levels, therefore, greatly simplify the preparation of the sizing composition, since only one starch derivative is needed.

Table III below shows the relationship between the percent pickup of octenyl succinate starch and the effect on sizing that the percent pickup has.

Table III

Percent Pickup Example 1 Starch	Hercules Sizing Test, Seconds (#2 INK)
3.0	27
6.0	80
9.0	122

Table III above clearly shows a dramatic increase of water resistance when the amount of pickup of the subject starch derivative is increased. Tripling of the pickup of the subject starch derivative causes a substantial increase in water resistance of the sheet, as evidenced by the Hercules Sizing Test results (122 seconds). The above sizing effect was obtained without the use of any rosin in the wet-end, but in some applications, it may be desirable to include a small amount(1-1.5 kg rosin/tonne of paper furnish) in the wet-end to aid in controlling size press pickup.

As pointed out earlier, to obtain effective sizing, it is a requirement of the method of the present invention that some alum (aluminium sulphate) or sodium aluminate be added at the wet-end, so that there is actually a minimum amount of aluminium ion in the paper web as it enters the size press. At the present time, it has been found that about 5 kg alum/tonne of fibre in the paper web is the minimum required to obtain effective water-resistant sizing in the finished paper sheet.

The subject starch derivative is cooked prior to application to the sheet, either by batch methods, or by a continuous cooking method, such as jet cooking. The subject starch derivative can be combined with a conventional size press starch (e.g. pearl cornstarch) to increase the strength of the sheet. The application temperature should not fall below 51°C., and is preferably in the range of 76-82°C. For best pickup and sizing at the size press using the subject starch derivative, a pH in the wet-end of about 4-6 has been found to be desirable.

The subject starch derivative is most useful when added at the size press to develop a high degree of water resistance in a paper web which contains alum, sodium aluminate, or other multivalentmetal ion introduced at the wet-end of the papermaking machine. The starch derivative also develops internal strength equivalent to the most efficient of the conventional size press starches. It is also contemplated that the subject starch derivative can be applied to a cellulosic sheet from a calender stack to efficiently obtain a higher level of water resistance in such sheets.

The viscosity characteristics of this starch are described below. As the concentration increases from a 2% dsb starch to 12% dsb starch, the Brookfield viscosity increases. For example, at 52°C, the Brookfield viscosity of a 2% dsb aqueous starch sample was about 13 cps. When the concentration was increased to 8%, the Brookfield viscosity was about 45 cps., at 10% concentration, the Brookfield viscosity was about 69 cps. and at 12% starch concentration, the Brookfield viscosity was about 97 cps. As the temperature is increased, the viscosity increases with increased solids levels are not as large as they are at lower temperatures. For direct comparison of the temperature effect see the table below:

TABLE IV

EFFECT OF STARCH CONCENTRATION AND TEMPERATURE ON BROOKFIELD VISCOSITY

Percent Starch Concentration	Temperature		
	52°C	66°C	79°C
2	13 cps	11.8 cps	11.8 cps
8	45 cps	36.0 cps	28.0 cps
12	97 cps	73.0 cps	53.0 cps

The above Brookfield viscosities were obtained using a #1 spindle at 100 rpm.

The above viscosity/solids/temperature characteristics are typical of size press starches. It is considered desirable that the subject starch have such viscosity characteristics for convenience of application, particularly when it is applied from the size press in combination with other conventional starches.

Although the exact reason is not known with certainty, the subject starch derivative is not effective when subjected to viscosity thinning by means of enzyme conversion. It is possible that the enzyme separates the octenyl groups from the starch ester, so that the hydrophobic properties are lost.

Other starch ester derivatives are also believed to be useful in the method of sizing paper at the size press to obtain high levels of water resistance. These additional starch derivatives may be made from substituted cyclic dicarboxylic acid anhydrides and mixed anhydrides which attach to the starch molecule through the ester group, have hydrophobic properties, and are capable of reacting with the multivalent metal ion (aluminium ion) in the paper web as it passes through the size press. It is contemplated that hydrocarbon chain extensions obtainable from C_6-C_{24} cyclic dicarboxylic anhydrides are useful for this purpose with the necessary adjustments in concentration of the respective starch derivatives in the size press dispersion. For extremely hydrophobic starch derivatives, less will be required to obtain water resistance, and in those instances, a more conventional size press starch is used to obtain internal strength in the paper sheet.

<u>EXAMPLE 4</u>

One hundred parts of cornstarch is slurried in water in about 22.5° Bé at 16°C. The slurry temperature is then raised to about 32-35°C, and the pH is adjusted to about 6.5-7.0 with 5% (7.0-7.4° Bé) sodium hydroxide solution. Then about 2% by weight based on the starch weight, of 1-octenylsuccinic anhydride is added to the slurry with agitation (as rapidly as possible). As soon as all the anhydride is in, the addition of 5% (7.0-7.4°Bé) sodium hydroxide is begun, and the pH of the slurry is adjusted to 6.5-7.5. The addition of sodium hydroxide is continued with agitation for about 2½ hours with constant agitation while the pH of the slurry is maintained at about 6.5-7.5 with 5% sodium hydroxide. The reaction is continued until the pH remains constant. The degree of substitution at completion of the reaction should be in the range of 0.008 to 0.016.

The pH of the derivatized starch slurry is then adjusted to 5.5-6.0 and temperature is adjusted to 43°C. The resulting product is then screened, filtered, washed and dried. The resulting product should have the following characteristics:

Moisture - 10-13%
pH - 6-7
d.s. 1-octenylsuccinate - 0.008-0.016

The above starch derivative is not thinned, but should be, prior to use. It can be thinned at the paper mill at the time of use by thermal-chemical cooking as described in Example 6 below.

EXAMPLE 5

One hundred parts of cornstarch is slurried in water to a solids level of about 22.5° Bé at 16°C. The slurry pH is adjusted to about 7.5 with anhydrous sodium carbonate, and the slurry temperature is adjusted to 49-52°C. The slurry is then subjected to alkaline bleaching for about two hours using about 1.7% by weight of NaOCl, or about 0.5% by weight chlorine (based on the weight of the starch). The alkali fluidity of the bleached starch should be at least 65 ml. using a 2.5 g. sample, 0.375N and the test procedure described following the examples. The bleaching step is terminated by adding 0.13% by weight, based on the total starch weight, of sodium bisulphite.

The slurry temperature is adjusted to about 32-35°C and the pH is maintained in the range of 6.5-7.0. Then about 2% by weight 1-octenylsuccinic anhydride is added while the slurry is vigorously agitated. Then sodium hydroxide is immediately added to adjust the pH to 6.5, and thereafter maintain the pH in the range of 6.5-7.5, and the esterification reaction is continued for about 2½ hours to the end point, during which the pH is adjusted with NaOH as needed to maintain the pH in the range of 6.5-7.0. The amount of 1-octenylsuccinic anhydride is limited to a total of 3% based on the dry substance weight of the starch. The slurry temperature is then adjusted to 43°C., followed by screening, filtering and drying. The dry product should have the following properties:

alkali fluidity: 75 ml. minimum (2.5 g sample, 0.375N)
d.s. of octenyl succinate groups: 0.008-0.016
(range 1-3% by weight octenyl succinate groups, based on starch)

The preferred degree of substitution level is 0.008-0.016 of octenyl succinate groups. However, the level of substitution may be as low as 0.005 or as high as 0.023, and still provide the benefits of increased sizing to some papers.

The starch half ester of Example 5 is also thinned prior to use, as described in Example 4, by thermal-chemical cooking, jet cooking, high temperature pressure cooking, acid hydrolysis, or by any conventional method, except enzyme thinning, to produce a thinned viscosity starch having a Brookfield viscosity in the range of 10-150 cps. (2-15% solids level; 66°C; No. 1 spindle at 100 rpm.). When the starch derivative has been bleached, as in Example 5, then chemical conversion at the mill is unnecessary. The bleached product produces better colour in the coated paper, also.

The viscosity of the starch composition is adjusted to effect the most desirable pickup of materials from the size press. There are viscosity differences dictated by particular paper machine apparatus, and also by the particular grade of paper being manufactured. For certain hard-to-size papers, it is believed that it would be desirable to increase the substitution level above the normal upper limit of

0.023, up to about 0.039. Such a starch derivative is then thinned, and can be used alone at the size press without a second, or supplementary, starch sizing agent. The pH range at the wet end may be up to 6, and, at the size press, the pH may range from 4 to 7.5.

The subject starch derivatives can be used without any rosin present in the wet end. However, it may be desirable to use about 1-1.5 kg. of rosin/tonne of paper in the wet end furnish of the paper making machine to help control size press pickup and to improve runability of the paper making process.

Sizing efficiency has been observed to fall off as the alum dosage in the wet end is lowered, and as the wet end pH is increased. Although, alum (aluminium sulphate) is presently preferred, it is also contemplated that other compounds can be substituted. Sodium aluminate, for example can be used to provide multivalent aluminium ion in the paper web as it enters the size press. In addition, it is expected that $CaCl_2$, $MgCl_2$, $MnCl_2$, or $BaCl_2$ could be used in the wet end furnish to provide a multivalent metal ion in the web of the paper entering the size press. At the present time, it appears that 5 kg. alum/tonne of fibre in the paper web is the minimum required to obtain effective sizing.

As pointed out above, it has been found that enzyme thinning of the octenyl succinate ester of starch is not an effective or desirable mode of thinning the starch derivative. Apparently, the octenyl succinate groups are cleaved away from the starch molecules by the enzyme action, and the starch derivative loses its effectiveness for sizing.

EXAMPLE 6

The starch ester derivative made according to Example 4 was tested under laboratory conditions to simulate application to a paper web at the size press of a paper making machine. Six hundred grams of the Example 4 starch derivative was slurried in sufficient water with 0.2%

ammonium persulphate based on the starch (dry substance weight) to make a total weight of 4000 g. The above slurry was then cooked at about 157-160°C through a loop type cooker similar to that described in U.S. Patent 3,661,640. The solids level of the cooked starch paste was 13% at a pH of 4.9. The pH was then adjusted to 5.7 with 5% NaOH solution. The solids of the cooked starch paste was adjusted to 10%. The Brookfield viscosity, using a No.1 spindle at 20 rpm. and 66°C was 35 cps.

A base sheet containing no rosin and 10 kg alum/tonne of paper was sized with the above starch derivative paste at 10% solids level and a pH of 5.7. The pickup of sizing calculated to 6.2%, which was considered excellent. The Hercules Size Test for the above sized paper was 49.5, indicating excellent sizing was obtained.

EXAMPLE 7

The starch ester derivative of Example 5 was also tested in the laboratory as described above in Example 6. The lightly oxidized starch derivative was first subject to thermal cooking (without added ammonium persulphate). A 15% solids slurry of the Example 5 starch derivative was jet cooked at a temperature of about 160°C in a jet cooker (without a loop tube). The solids level of the cooked starch derivative was adjusted to 10% by adding hot water. The Brookfield viscosity was 23 cps. (No. 1 spindle; 20 rpm; 66°C). The pickup of the cooked starch paste was 6.2%. The Hercules Sizing Test value was 85.6, showing unexpectedly superior sizing. Several additional runs were made and, although the Hercules Sizing Test for these runs were not as high as the initial run reported above, they were significantly better than tests made with a similarly substituted starch which had not been first slightly oxidized. A possible explanation for the superior performance of the starch derivative of Example 5 is that the light bleaching further reduces the protein content of the starch to less than about 0.1%. Lower protein levels and the carboxyl groups added by bleaching enhance film-forming properties of the starch. However, the carboxyl content is kept below 0.3% because excessive carboxyl groups from recycled broke act as a dispersant in the wet end of the paper machine and thereby interfere with filler retention. Wet end problems are avoided by limiting the amount of carboxyl groups on the starch derivative used at the size press.

TEST PROCEDURES

Determination of Degree of Substitution

The d.s. of octenyl succinate may be measured by determining the carboxyl level of the unsubstituted starch, and subtracting this value from the carboxyl level determined on the reacted and filtered starch. The determination may be made by titrating known samples with standard (0.100N) sodium hydroxide to pH 7.5. The respective samples are thoroughly washed prior to the test, to remove any unreacted reagent from the product test sample, and to subject the control to all the same conditions as the test sample.

ALKALI FLUIDITY

The alkali fluidity or "inhibition index" test is substantially as described in United States Patent 3,876,629, column 7, lines 33-67 and column 8, lines 1-10.

HERCULES SIZING TEST

This test is described in Hercules Sizing Tester Instruction Manual HST-1A using Model KA Hercules Sizing Tester sold by Hercules, Inc. of Wilmington, Delaware, U.S.A. The results are all obtained using a Hercules No.2 ink and 80% reflectance.

MULLEN STRENGTH TEST

This test is described in TAPPI Standard T403 os-76 (Technical Association of the Pulp and Paper Industry).

CLAIMS

1. A method of externally sizing a cellulosic web containing a multivalent metal ion to impart increased water resistance to the web by applying an aqueous sizing composition to the cellulosic web, characterised in that the aqueous sizing composition contains from 2 to 15% by weight of a dicarboxylic acid starch ester obtained by reacting starch with a dicarboxylic acid anhydride having 8 to 22 carbon atoms which is an aliphatic, aromatic, alicyclic, or bicyclic aliphatic dicarboxylic acid anhydride, the said starch ester having a degree of substitution of the dicarboxylic acid anhydride in the range from 0.005 to 0.023 in that the aqueous sizing composition has a Brookfield viscosity in the range of 10 to 150 cps (No.1 spindle; 20 rpm; 66°C), in that the sizing composition has a pH of 4 to 7.5 and a temperature of 50 to 80°C, and in that the sizing composition is applied to the cellulosic web at a rate of 10 to 100 kg per tonne.

2. A method as claimed in claim 1, characterised in that the starch ester is obtained b y reacting starch with 1-octenyl succinic acid anhydride.

3. A method as claimed in claim 2, characterised in that the starch ester is a 1-octenylsuccinic acid half ester of cornstarch, the degree of substitution of which is in the range of 0.008 to 0.016.

4. A method of claim 3, characterised in that the 1-octenylsuccinic acid half ester of cornstarch is slightly oxidized so that the amount of protein remaining in said half ester is less than 0.1% by weight based on the weight of the starch.

5. A method as claimed in any of claims 1 to 4, characterised in that the multivalent metal ion is aluminium calcium, magnesium, manganese or barium.

6. A method as claimed in claim 5,characterised in that the multivalent metal ion is in the form of a slightly water-soluble salt, and is added to the aqueous furnish from which the cellulosic web is formed.

7. A method as claimed in claim 6, characterised in that the multivalent metal salt is aluminium and is obtained from aluminium chloride, aluminium sulphate or sodium aluminate.

8. A method as claimed in claim 7, characterised in that the multivalent metal salt is aluminium sulphate which is present in the cellulosic web in an amount of at least 5 kg aluminium sulphate per tonne of fibre in the cellulosic web, or in that the multivalent metal salt is sodium aluminate which is present in the cellulosic web in an amount of at least 1.5 kg. per tonne of fibre in the cellulosic web.

9. A method in any of claims 1 to 8 characterised in that the reduced viscosity of the starch ester is obtained by acid hydrolysis of the starch ester or by thermal-chemical treatment of the starch ester.

10. A method as claimed in any of claims 1 to 8, characterised in that the substituted starch has been slightly oxidized, and the reduced viscosity is obtained by high temperature thermal treatment.

11. A method as claimed in claim 10, characterised in that the temperature of the thermal treatment is in the range 107 to 163°C.

12. A method as claimed in any of claims 1 to 11, characterised in that the paper web is free of rosin.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 80 30 0078

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 2 370 772 (NATIONAL STARCH AND CHEMICAL) * Claims 1-13; examples II,IV *	1,2,5-8
D	& JP - A - 53 061 706	
	--	
	FR - A - 2 303 114 (NALCO) * Claims 1,3; examples 3,4 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})

D 21 H 3/28
D 21 D 3/00

TECHNICAL FIELDS SEARCHED (Int.Cl. ^{3})

D 21 D 3/00
D 21 H 3/28

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☑ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15-04-1980	NESTBY

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