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(54) Process for the manufacture of paper, paper additive composition and paper of improved surface properties.

(57) This invention discloses a process for the manufacture of paper having retained therein high levels of starch wherein such starch is a specially treated, cooked, cross-linked starch which is added with a poly-electrolyte at the wet end of the paper manufacturing process or sprayed on the web in the paper-forming process. The invention also relates to a novel wet-end paper additive composition which includes the specially treated, cooked, cross-linked starch and a polyelectrolyte and the improved paper produced therefrom.

Croydon Printing Company Ltd.

This invention relates to use of a cooked, specially-treated starch product as a paper wet-end additive for the elimination of conventional surface sizing.

Although a small amount of high grade paper is manufactured from rag pulp, paper is manufactured for the most part from wood pulp. There are five different kinds of wood pulp: mechanical pulp (ground wood), semi-chemical pulp, sulfite pulp, sulfate or kraft pulp, and soda pulp. The first is prepared by purely mechanical means, the second by a combination of mechanical and chemical means, and the other three by chemical means. The mechanical pulp contains substantially all the wood except the bark and that lost during storage and transportation. Semi-chemical pulps are partially free of lignin. Chemical pulps, however, are essentially cellulose, the unwanted lignin and other non-cellulosic components of the wood having been dissolved away by the cooking and bleaching treatment. Because of this, chemical pulps are much superior to mechanical and semi-chemical pulps for fine paper making. However, because of the special processing required, they are too expensive to serve as a main source of fiber for the cheaper grades of paper such as newsprint.

If the pulp fibers were the only constituents of a paper sheet, the usefulness of the paper would be very restricted because the sheet would be soft, have a yellowish color, and could not be successfully written or printed upon with ink. If the sheet were thin, it would be transparent to matter printed upon the opposite side. It is necessary, then, to add other substituents, such as sizing or coloring agents and fillers to the cellulosic fibers to produce papers suited to its many uses.

Many papers, except the absorbent types, filter papers and most packaging papers, must have a finely ground filler added to them, the purpose of which is to occupy the spaces between the fibers - thus giving a smooth surface, a more brilliant whiteness, improved printability and improved opacity. Sizing is added to the paper, other than absorbent papers and filter paper, to impart resistance to penetration by liquids. Common sizing agents added to the pulp before it is formed into a sheet are wax emulsions or soaps made by the saponification of rosin with alkali. The sizes are precipitated with alum. Such sizing as described in this paragraph is known in the trade as internal sizing.

The word sizing is also used in a second context in the paper industry. This second use is known as surface sizing. It differs from the internal sizing previously described in that it is applied to the surface of the paper where it cements the fibers to the body of the paper and deposits a more or less continuous film on the paper surface. Surface sizing is used to produce a smooth hard surface which will not catch a pen when the paper is written upon, will not pick off if the paper is printed using tacky inks and will not show feathering of the ink. An additional advantage of a surface size is that oil resistance of the paper is improved since the size tends to seal the pores of the paper. Surface sizing may be of greater importance than internal sizing for certain types of papers such as writing papers, printing papers and some wrapping papers. It is important to surface size paper that is used in an offset printing process since this prevents loosening of surface fibers when the paper is moistened with water on the press.

A common way to add a surface size is to apply the sizing agent to both sides of the paper when the paper is passed through press rolls on the paper machine. These rolls force the size into the paper and remove excess size from the surface of the paper. Inherent in this process are various mechanical problems which make it expensive to apply and maintain a uniform layer of the size on the surface of the paper. This mechanical equipment is costly, and there is the added expense of evaporating the water added to the paper with a dilute suspension of the size. Commonly the size is a starch or a starch derivative such as an hydroxyethyl starch.

Starch has long been used as an additive in the manufacture of paper to strengthen the paper sheet. See for example Whistler and Paschall, Starch: Chemistry and Technology, Academic Press Inc., New York, N.Y. Vol. 2, 1967, Chapter VI. For this purpose, starch is added to the pulp before the paper sheet is formed. The starch is usually cooked in water before the mixture is added to the pulp. This procedure produces much soluble material which is not effectively retained in the paper sheet. An improvement in starch cooking was disclosed in U.S. Patent 2,805,966, issued September 10, 1957, wherein the starch slurry was heated in a steam injection cooker. This permitted control of the heating so that the majority of the starch granules were swollen but not ruptured. However, the temperature range over which the granules of starch swell and gelatinize is large. Even in this process only a portion of the granules can be obtained in the desired swollen state. Some starch granules may be still unswollen and hence useless as an adhesive while others are solubilized and not retained in the starch. Furthermore, many of the swollen starch granules so prepared have a tendency to disintegrate and form more solubles when their slurries in water are subjected to vigorous agitation.

One method to obtain a starch whose swollen granules do not disintegrate during agitation was disclosed in U.S. Patent 2,113,034, issued April 5, 1938. This was accomplished by reaction of starch with formaldehyde. The product is resistant to dispersion in hot water, and requires treatment with alkali and vigorous beating to render the starch suitable as a paper pulp additive. As a result of these treatment requirements and because the starch is only partially retained in the paper sheet, the product has never found acceptance in the paper manufacturing industry.

A second method to obtain a starch whose swollen granules would not disintegrate during agitation was disclosed in U.S. Patent 2,328,537, issued September 7, 1943. This was accomplished by reacting the starch with certain antimony or phosphorous chlorides or oxychlorides. The patent suggested that the products might be useful in the manufacture of paper. Again, these products have never found acceptance in the paper manufacturing industry, because the products described show limited swelling in hot water and are only partially retained in the paper sheet.

One method which partially overcomes these difficulties is disclosed in copending U.S. Application, Serial No. 780,614, filed March 23, 1977, which is incorporated in this application by reference. This method employs a specially-treated starch whose granules swell to a desired degree in cold water. This modification eliminates the need for specially controlled heating of the starch as required in the prior art but it still necessitates pretreatment of the starch under carefully controlled conditions.

It would therefore be an advance in the art if an additive were discovered which could be incorporated into the paper pulp prior to sheet formation that would impart improved surface properties to the paper. This would avoid the necessity for a separate surface sizing step with the attendant addition of moisture and the necessity of further drying of the product. Moreover, if such surface properties could be imparted without imparting detrimental side effects, and loss of desirable properties, the additive in question would find ready acceptance in the art. If on the other hand, properties of the finally formed paper article, such as dry strength and tensile strength were improved by means of the additive, this would be an added economical benefit to be gained through use of an additive of this type.

It is therefore an object of the invention to provide a new and improved method for imparting the characteristics of surface sizing to manufactured paper by the addition of a specific additive to the pulp during the paper processing.

A further object is to provide an agent of this type to improve surface properties without interfering with the other additives and substances used in the makeup and manufacture of paper and without showing adverse effects on the chemical and physical characteristics of the finished sheet.

Another object of the invention is to provide an additive for improving surface properties which is retained in and not washed out of the paper in the sheet forming process.

An important object of the invention is to provide an additive for improving surface properties of manufactured paper which will operate on a wide variety of paper stocks, is safe to handle and will impart to the finished sheet desirable characteristics which have not heretofore been available when prior art attempts have been made to make paper without the additional separate step of applying a coating of surface size. A specific object of this invention is to provide a method of improving surface properties of manufactured paper by the addition of a specific additive to the wet-end which also imparts to the finished paper article improved dry strength.

A still further object of this invention is to provide a starch additive for paper that is readily prepared, whose granules swell in hot water to the desired degree without the need to carefully control the heating conditions, and whose swollen granules do not disintegrate when subjected to vigorous agitation.

This invention relates to an improved process for the manufacture of paper which comprises the steps of:

(a) adding an aqueous suspension of a cooked, cross-linked starch having a cooked swollen volume (hereafter referred to as CSV) of from about 4 ml/g to about 25 ml/g to an aqueous suspension of cellulosic pulp;

(b) adding a polyelectrolyte to the starch-pulp mixture; and

(c) forming paper from said mixture of pulp, starch and polyelectrolyte.

Another aspect of this invention is a wet-end paper additive composition which comprises:

(a) an aqueous suspension of a cooked, cross-linked starch having a CSV of from about 4 ml/g to about 25 ml/g; and

(b) a polyelectrolyte.

The present invention also is directed to an improved process for the manufacture of paper which comprises spraying an aqueous suspension of a cooked, cross-linked starch having a CSV of from about 4 ml/g to about 25 ml/g onto the wet web in the paper-forming process and drying such web.

In accordance with this invention, it has been discovered that certain cross-linked starches which show a specific degree of swelling in hot water impart excellent surface properties to manufactured paper when they are added to the pulp in the paper-making process. The paper so obtained compares very favorably with surface-sized papers manufactured by the expensive surface sizing process. Furthermore, the process gives a finished paper with improved dry strength. The incorporation of the cross-linked starches of this process does not interfere with the other additives and substances used in the makeup of the manufacture of paper. There are no adverse effects on the chemical and physical characteristics of the finished sheet.

The starch reactant itself that may be used in practicing the invention may be derived from any vegetable source such as for example corn, wheat, potato, tapioca, rice, sago and grain sorghum. It may be either waxy or nonwaxy. The term starch is used broadly herein and encompasses unmodified starch and tailings, and as well, starch that has been modified somewhat by treatments with acids, alkalies, enzymes or oxidizing or derivatizing agents. If the starting starch is modified or derivatized in some manner, it nevertheless is useful as long as the product is still in the granular form and still contains hydroxyl groups capable of reacting with the cross-linking reagents.

The cross-linking agents used in this invention may be any of the well-known organic or inorganic polyfunctional reagents which can react with two or more starch hydroxyl groups. Examples of such reagents that are well known in the art are phosphorous oxychloride, sodium trimetaphosphate, epichlorohydrin and acrolein.

The cross-linked starches of this invention may be prepared by the general procedure disclosed in U.S. Patent 2,328,537, issued September 7, 1943. It is necessary to control the cross linking carefully to obtain a suitable product. Suitable products for this invention are those which when cooked in water give a CSV of from about 4 to about 25 ml/g, preferably about 7 to about 20 ml/g. CSV is measured as follows:

To 10.00 g dry basis of starch in a 600-ml stainless steel beaker is added 190.0 g of distilled water. Cover with a watch glass having a center hole for a stirring shaft. Stir at 500 rpm for 18 min in a boiling water bath. Cool to 28°C by stirring in a cold water bath. Add distilled water to exactly replace the water lost by evaporation, transfer to a 250-ml centrifuge bottle and centrifuge at 2000 rpm for 10 min. Mark the level of the paste in the bottle. To determine solubles, a weighed aliquot of the supernatant liquid is evaporated on a steam bath. Then the residue is dried for 4 hours at 120°C in a vacuum oven and weighed. The per cent solubles is calculated as follows:

$$\text{\% Solubles} = \frac{\text{Weight of Residue x 1900}}{\text{Weight of Aliquot}}$$

The volume the paste occupied in the centrifuge bottle is measured in milliliters. The CSV is calculated as follows:

$$\text{CSV} = \frac{\text{Paste Volume in ml}}{\text{Insoluble Weight in g}}$$

$$\left[\text{Where Insoluble Weight} = 10.00\left(1 - \frac{\text{\% Insolubles}}{100}\right)\right]$$

If no layer of paste separates after centrifugation, the test is repeated using a 5-g sample of starch with corresponding adjustment in the calculations.

It has been found that products with a suitable CSV are obtained when starch is treated with from about 100 to about 2000 micromoles of $POCl_3$ per mole of starch. (A mole of starch is defined as 162 g of starch on a dry basis, the weight of one anhydroglucose unit of the starch.) Suitable amounts of other cross-linking agents are readily determined by experimentation.

Starches with the CSV specified above give, when cooked in water, swollen granules particularly useful in the paper-making process. Use of these cross-linked starches obviates the need for carefully controlled heating of the starch slurries as was required in the prior art processes. Furthermore, it has been found that the swollen granules prepared from the cross-linked starches with the specified CSV have little or no tendency to disintegrate when subjected to vigorous agitation.

The starch is prepared for addition to the paper pulp by cooking a suspension in water. Cooking may be accomplished in a batch cooker or a jet cooker. The cross-linked starch, properly cooked in water, may be added to the paper furnish at various points in the operation where there is efficient mixing. A suitable point of addition is at the suction side of the fan pump.

The starches of the present process are effective when used at levels of about 1% to about 20% by weight of dry solids in the mixture of starch and pulp. The preferred use level is from about 5% to about 10% by weight of dry solids in the mixture. It has been discovered that such cross-linked starches are well retained and that when used at the preferred use levels less than about 20% of the starch added is lost from the paper in the sheet-forming process if a polyelectrolyte is added to the mixture following the addition of the starch. The surprising finding is that such polyelectrolytes, which have been used previously for the retention of mineral pigment in the paper, are effective in promoting the retention of the cross-linked starches. Such polyelectrolytes may be used at a level of about 0.01% to about 1%, preferably at a level of about 0.025% to about 0.1% by weight of the dry weight of furnish. The polyelectrolyte is added to the pulp at a point in the process after the cross-linked starch has been added.

The polyelectrolytes employed in the process of this invention may be those employed by paper makers as flocculating agents or as aids to improve the retention of pigments in the paper. They may be either anionic or cationic. Examples of those which are suitable are the acrylamide-based copolymers sold by the Hercules Corporation, Wilmington, Delaware, under the Reten trademark; those sold by the Nalco Chemical Company, Oak Brook, Illinois, under the Nalco trademark; and those sold by the Betz Laboratories, Trevose, Pennsylvania, under the Betz trademark.

The best polyelectrolyte for use in a particular paper-making system is determined by the following method:

> In a Britt Dynamic Drainage Jar, distributed by Paper Research Materials Co., 770 James St., Apt. 1206, Syracuse, N.Y. 13203, is placed 500 ml of prepared furnish. The mixture is agitated at 700-800 rpm for 15 seconds before the required amount of polyelectrolyte is introduced. The mixture is agitated for an additional 10 seconds before the clamp is opened and 100 ml of filtrate is collected. The filtrate, diluted if necessary, is placed in an electrophotometer and per cent transmission is determined at 425 mμ. The polyelectrolyte which gives the highest transmission in this test is the best polyelectrolyte for use in the particular system tested.

In a separate embodiment of this invention, it has been discovered that the starches of this invention may be sprayed onto the wet web in the paper-making process. Papers produced by this method exhibit excellent surface properties comparable with those of surface-sized papers. This process also avoids the necessity for a separate surface sizing step with the attendant addition of moisture and the necessity of further drying of the product.

The following examples further illustrate the practice of this invention. It should be understood, however, that the invention is not limited to the examples given below.

EXAMPLE I

Cross-linked starches were prepared using 400, 800 and 1600 micromoles of phosphorous oxychloride per mole of commercial corn starch. Paper handsheets were prepared incorporating these cross-linked starches by the following procedure. The starch was cooked by heating a stirred 5% slurry in water for 15 minutes at 95-100°C. The starch slurry was added to the paper pulp prepared from a 50/50 bleached hardwood/softwood kraft pulp. The pulp also contained alum in the ratio of 2% by weight of the dried pulp. There was added 0.1%, based on total solids weight, of a polyelectrolyte, Reten 421. The pH of the pulp slurry was adjusted to 4.5 with sulfuric acid before the starch was added. The dilute pulp slurry containing approximately 3% by weight solids was used to make paper handsheets using a Williams sheet machine for a series of 4 sheets formed continuously, pressed and dried. Blank sheets were prepared using the same pulp-alum composition without the addition of any starch. Bursting strength (Mullen points), critical wax pick and K & N ink holdout tests were measured by TAPPI (Technical Association of the Pulp and Paper Industry, 360 Lexington Avenue, New York, New York 10017) Methods T403ts-63, T459su-65, UM413, respectively. The data are summarized in Table I.

This Example shows that the addition of a cooked, cross-linked starch to paper pulp improves the dry strength, wax pick and ink holdout of the paper.

TABLE I

PAPER HANDSHEET PROPERTIES

10% CROSS-LINKED STARCH - 90% MIXED BLEACHED KRAFT PULP

Starch[a)]	Mullen Bursting Strength, (pts)	Critical Wax Pick[b)]	K & N Ink Holdout[c)]
400 micromole $POCl_3$ XL Corn	18.5	16	55.1
800 micromole $POCl_3$ XL Corn	13.0	10	57.0
1600 micromole $POCl_3$ XL Corn	11.5	9	58.5
400 micromole $POCl_3$ XL Waxy Corn	18.5	16	48.3
Blank Sheets (Control)	10.0	7	59.3

a) XL = Cross-Linked.

b) Average of determinations on at least two sheets.

c) Average of three determinations.

EXAMPLE II

The procedure of Example I was repeated using the cross-linking agent at a level chosen to give starch with a CSV in the preferred range. The cross-linking agents used were epichlorohydrin, sodium trimetaphosphate, and phosphorous oxychloride. The starches were used at the 10% level as in Example I. Results are given in Table II.

This Example shows that various cross-linking agents are equally effective in producing cross-linked starches which improve the properties of paper.

TABLE II

PAPER HANDSHEET PROPERTIES

Starch Cross-Linking Reagent	CSV (ml/g)	Mullen Bursting Strength (pts)	Critical Wax Pick[a)]
None	--	11	8
Phosphorous Oxychloride	14	22	16
Sodium Trimetaphosphate	14	22	16
Epichlorohydrin	11	22	16

a) Average of determinations on at least two sheets.

EXAMPLE III

Tests were run on a pilot paper machine using a pulp furnish that was 50% bleached hardwood kraft and 50% bleached softwood kraft mixture beaten to a 450 ml Canadian standard freeness. Fortified rosin size (1%) and alum (2%) were added to the pulp in the beater. Starch was cooked in water using batches of 9.1 kg starch and 143 kg water. The cooked starch and pulp were mixed together in the machine chest at a 2% by dry weight of furnish consistency. The paper machine was run at a speed of 27.4 m/min using 72.6 kg/hr of pulp to make 66.6 g/m^2 basis weight paper. A 0.75% aqueous solution of Reten 421, an anionic polyelectrolyte, was added at a standpipe just prior to the fan pump. Addition was made at such a rate as to give a concentration of the polyelectrolyte of 0.05% by dry weight of the total solids. All paper was calendered three nips on the paper machine calender stack.

A surface-sized control paper was made using an 0.07 degree of substitution, 80-fluidity hydroxyethyl starch, applied as a surface size. This was cooked at 15% commercial moisture basis solids and diluted to 10% solids for size press application. There was 4% pickup of this starch on the paper. Results of the experiments are given in Table III.

The IGT Printability Test was performed according to TAPPI Method T499su-64. The porosity and smoothness tests were performed according to TAPPI Methods T460m-49 and 479sm-48, respectively, and employed the Gurley-Hill S-P-S Tester, manufactured by Gurley Testing Instruments, Troy, New York. The amount of starch retained in the paper is determined as follows:

Prepare $CaCl_2$ solution by dissolving 540 g of $CaCl_2 \cdot 2H_2O$ in water and dilute to 1 liter. Adjust the specific gravity to 1.30 at 16°C with water. Adjust the pH to 1.8 with glacial acetic acid.

Prepare a $UO_2(C_2H_3O_2)_2$ solution by dissolving 10 g of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ in 80 ml water and 20 ml glacial acetic acid. Do not heat above 60°C. Dilute with 100 ml of the $CaCl_2$ solution.

Weigh accurately a 2-g sample of paper cut into pieces approximately 1 cm square. Macerate in 10 ml water in a 250-ml beaker. Add 60 ml $CaCl_2$ solution and boil vigorously for 30 minutes with occasional stirring. Add water as needed to maintain a constant liquid level. Transfer quantitatively the cool mixture into a 100-ml Kohlrausch flask containing 10 ml of $UO_2(C_2H_3O_2)_2$ solution. Dilute to volume with $CaCl_2$ solution. Filter by gravity through an 18.5-cm retentive paper into a dry flask, discarding the first portion of filtrate. Determine the optical rotation of the sample in a 2-dcm polarimeter tube.

$$\% \text{ Starch} = \frac{\text{Degrees Angular Rotation} \times 100 \times 100}{2 \text{ dcm} \times 203 \times \text{Sample Weight (g)}}$$

Where: 203 = specific rotation of pure corn starch

This example shows that the cooked cross-linked starches of this invention when added to the paper pulp give paper with properties as good as or better than those of surface sized paper. They also show that the starches of this invention are well retained within the paper when they are added to the pulp with a polyelectrolyte.

TABLE III

Run No.	% Starch	Mullen Bursting Strength (pts)	Critical Wax Pick No.[c]		K & N Ink Holdout[d]		IGT Printability cm/sec Pick Failure		Smoothness sec to Pass 50 cc Air Between 8 Plies of Sheets[d]	Porosity sec to Pass 100 cc Air Through Sheet[d]	% Starch Retained
			Wire	Felt	Wire	Felt	Wire	Felt			
1	None (Blank)	18.0	12	12	43.9	42.4	30	25	16.6	22.6	-
2	Surface Sized Control	25.4	16	18	33.1	37.8	105	115	24.4	35.9	-
3	7[a]	26.1	18	18	38.7	36.7	125	125	17.1	50.5	100
4	10[a]	25.9	16	18	36.4	33.2	115	130	22.9	83.6	80
5	10[b]	27.4	18	16	39.1	35.6	120	155	17.1	77.6	82

a) Cross-linked starch with a CSV of 14 ml/g prepared using 400 micromoles of $POCl_3$ per mole of corn starch.

b) Cross-linked starch with a CSV of 12 ml/g prepared using 1000 micromoles of $POCl_3$ per mole of corn starch.

c) Average of two or more determinations.

d) Average of three determinations.

EXAMPLE IV

Handsheets were prepared using 50% bleached hardwood kraft and 50% bleached softwood kraft pulp. A $POCl_3$ cross-linked starch with a CSV of 14 was added at a level of 7% by dry weight of the starch pulp mixture. The furnish also contained 1% by weight dry basis of rosin and 2% by weight dry basis of alum plus a small amount of a polyelectrolyte added in dilute solution. Starch retention and handsheet properties are given in Table IV.

These results show that both anionic and cationic polyelectrolytes increase the retention in paper of the starches of this invention. Paper prepared with these additives has superior surface properties as measured by critical wax pick to those of paper prepared without these additives.

TABLE IV

HANDSHEET PROPERTIES AND STARCH RETENTION USING POLYELECTROLYTES

Polyelectrolyte					
Name	Charge	% in Furnish (Dry Basis)	Starch Retained (%)	Mullen Bursting Strength (pts)	Critical Wax Pick[a)]
None	—	—	60	22.2	14
Reten 421	Anionic	0.05	89	21.2	18
Betz 1215L	Anionic	0.10	85	20.1	18
Betz 1225L	Anionic	0.10	83	20.7	16
Nalco 625	Anionic	0.10	86	21.7	18
Nalco 7PD095	Cationic	0.10	71	22.8	16
Betz 1260	Cationic	0.10	80	23.8	18
	Blank Sheets (No Starch)			15.2	9

a) Average of determinations on at least two sheets.

EXAMPLE V

Paper handsheets were prepared from a pulp furnish containing 50% bleached hardwood kraft and 50% bleached softwood kraft. A 0.25% dispersion of starch in water was sprayed on the wet handsheet web while it was still on the wire. Sufficient material was sprayed on the paper to give a total addition of 2% starch by weight on a dry solids basis. Properties of the dried sheets are given in Table V.

These results show that the cross-linked starch of this invention, when sprayed on a paper web, imparts superior surface properties to the finished paper as measured by the critical wax pick.

TABLE V

SPRAYING OF STARCHES ONTO PAPER HANDSHEETS

Starch	Dispersion Method	Mullen Bursting Strength (pts)	Critical Wax Pick[a)]
$POCl_3$ Cross-Linked (CSV = 14)	Cooked at 100°C	13.8	14
80-Fluidity Hydroxyethyl	Cooked at 100°C	11.0	5
80-Fluidity Hydroxyethyl	Slurried	12.2	10
Unmodified Corn	Slurried	13.8	8
None	—	10.2	3

a) Average of determinations on at least two sheets.

Claims

1. An improved process for the manufacture of paper which comprises the steps of:

(a) adding an aqueous suspension of a cooked, cross-linked starch having a cooked swollen volume of from about 4 ml/g to about 25 ml/g to an aqueous suspension of cellulosic pulp;

(b) adding a polyelectrolyte to the starch-pulp mixture; and

(c) forming paper from said mixture of pulp, starch and polyelectrolyte.

2. The process of claim 1 wherein said cross-linked starch comprises from about 1% to about 20% by weight of the starch-pulp mixture on a dry solids basis.

3. The process of claim 1 wherein at least about 80% by weight of the cross-linked starch added to the pulp is retained in the paper.

4. The process of claim 1 wherein said polyelectrolyte comprises from about 0.01% to about 1% by weight of said pulp, starch and polyelectrolyte mixture on a dry solids basis.

5. The process of claim 1 wherein said polyelectrolyte comprises an anionic or cationic acrylamide based copolymer.

6. A wet-end paper additive composition which comprises:

(a) an aqueous suspension of a cooked, cross-linked starch having a cooked swollen volume from about 4 ml/g to about 25 ml/g; and

(b) a polyelectrolyte.

7. The composition of claim 10 wherein the polyelectrolyte comprises an anionic or cationic acrylamide based copolymer.

8. A paper of improved surface properties which comprises cellulosic fiber, a cooked, cross-linked starch having a cooked swollen volume of from about 4 ml/g to about 25 ml/g and a polyelectrolyte.

9. An improved process for the manufacture of paper which comprises spraying an aqueous suspension of a cooked, cross-linked starch having a cooked swollen volume of from about 4 ml/g to about 25 ml/g onto the wet web in the paper-forming process and drying such web.

10. The process of claim 9 wherein the amount of cooked, cross-linked starch added to the wet web is about 2% by weight of the dry basis weight of the furnish.