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(54) Title: GELLED STARCH COMPOSITIONS AND METHODS OF MAKING GELLED STARCH COMPOSITIONS

(57) Abstract: A starch composition is made by combining starch with a species which induces gelation, and cooking the starch before or after the combination, to produce a gel. The species which induces gelation is selected from the group consisting of the following species and combinations thereof. (a) one or more anionic, cationic or amphoteric inorganic colloidal species; (b) one or more species capable of ionic or coordination bonding; and (c) one or more species capable of hydrogen bonding. The invention also provides a dry starch composition suitable for forming an additive for a paper furnish. A method of making a starch composition is also provided.



WO 2005/004812 A2

GELLED STARCH COMPOSITIONS AND METHODS OF MAKING GELLED STARCH COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. provisional patent application serial number 60/484,095, filed July 1, 2003.

TECHNICAL FIELD

This invention relates to gelled starch compositions of the type suitable for use as a retention aid in the manufacture of paper, or as a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The invention also relates to methods for manufacturing such gelled starch compositions.

BACKGROUND OF THE INVENTION

Many additives have been recommended in the prior art for improving the retention of fine particles and other papermaking material and improving wet-end drainage. Starches and polyacrylamides are frequently used for this purpose.

U.S. Patent 6,451,170 (Anderson, et al.) discloses a cationized crosslinked starch and use of the starch that allows for modification to correspond to variations in the wet end of the papermaking machine.

Keiser, et al. reveal a method for increasing retention (U.S. Patent 6,361,653) and drainage (U.S. Patent) in papermaking with the use of borosilicates in conjunction with a high molecular weight synthetic flocculent and/or starch, with or without the addition of a cationic coagulant.

U.S. Patent 6,274,112 (Moffett, Simmons) present a continuous process for preparing silica microgels for use as a drainage and retention aid in paper making, as a flocculation agent in potable water purification plants, and in similar applications.

U.S. Patent 6,238,520 (Greenwood) discloses a coagulated slurry containing undissolved starch particles, cationic polymeric flocculant and anionic microparticulate network agglomeration aid, such as bentonite.

U.S. Patent 6,235,835 (Niessner, et al.) present a starch modified with at least one cationic polymer and the modified starch is prepared by a process in which a) an anionically modified starch is reacted with a cationic polymer or b) a natural starch or a starch which has not been anionically modified is reacted with the cationic polymer in the presence of an anionic modifier and the polymer-modified starch is used.

Burnfield (U.S. Patent 6,217,709) discloses a composition comprising of a cationic starch, cationic galactomannan gum and acid suitable as a drainage aid and strength additive.

U.S. Patent 6,168,686 (Sutman, et al.) present a novel method for improving drainage rate and retention of fines comprising of adding a cationic or amphoteric starch, and a cationic polyelectrolyte followed by the addition of a high molecular weight anionic polyacrylamide copolymer.

U.S. Patents 5,859,128 and 6,048,929 (Moffett, R.) disclose a paper furnish containing a modified starch prepared by cooking at least one amphoteric starch, or cationic starch with at least one polyacrylamide as the retention aid under alkaline conditions. U.S. Patents 5,482,693 (Rushmere, J., Moffett, R.), 5,176,891 (Rushmere, J.) and 4,954,220 (Rushmere, J.) present a process for producing water-soluble polyparticulate polyaluminosilicate microgels.

U.S. Patent 5,178,730 (Bixler, H., Peats, S.) discloses that an improvement in retention can be achieved by adding a medium/high molecular weight cationic polymer or by adding a natural hectorite to the furnish.

U.S. Patent 4,643,801 (Johnson, K.) reveals a binder comprising a cationic starch in combination with an anionic high molecular weight polymer and a dispersed silica to improve retention. Similarly, U.S. Patent 4,388,150 (Sunden, O., et al.) discloses that an improvement could be found with the use of colloidal silicic acid and cationic starch.

U.S. Patent 4,066,495 (Voight, J.; Pender H.) presents a method of adding cationic starch and an anionic polyacrylamide polymer to the pulp in a papermaking process to improve retention.

U.S. Patent 4,954,220 (Rushmere) reveals the use of anionic polysilicate microgels with an organic polymer to flocculate pulp and filler fines, to improve water removal and fines retention.

SUMMARY OF THE INVENTION

This invention relates to compositions obtained by cooking starch and combining the starch, before or after cooking with species which induce gelation. The resulting modified starch compositions may be used as a retention aid in the manufacture of paper or as a clarifying aid for removing solids and other suspending materials from an aqueous dispersion.

According to this invention there is also provided a starch composition made by cooking a starch and a species which induces gelation.

According to this invention there is also provided a starch composition made by cooking a starch, a polyacrylamide polymer and a species which induces gelation.

According to this invention there is also provided a starch composition made by cooking a starch, anionic or potential anionic polymer and a species which induces gelation.

According to this invention there is also provided a dry starch composition suitable for forming an additive for a paper furnish, the starch composition comprising a starch and a species which induces gelation.

According to this invention there is also provided a dry starch composition suitable for forming an additive for a paper furnish, the starch composition comprising a starch, a polyacrylamide polymer and a species which induces gelation.

According to this invention there is also provided a dry starch composition suitable for forming an additive for a paper furnish, the starch composition comprising a starch, an anionic or a potential anionic polymer and a species which induces gelation.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising combining starch (with or without polyacrylamide and/or an anionic or potential anionic polymer) and one or more anionic, cationic or amphoteric inorganic colloidal species to form a starch composition, and cooking the starch composition to produce a gel.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising cooking starch (with or without polyacrylamide) and combining the cooked starch with one or more anionic, cationic or amphoteric inorganic colloidal species with or without an anionic or potential anionic polymer, to form a gelled starch composition.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising combining starch (with or without polyacrylamide and/or a anionic or potential anionic polymer) and one or more species capable of ionic or coordination bonding to form a starch composition, and cooking the starch composition to produce a gel.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising cooking starch (with or without polyacrylamide) and combining the cooked starch with one or more species capable of ionic or coordination bonding with or without an anionic or potential anionic polymer, to form a gelled starch composition.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising combining starch (with or without polyacrylamide and/or a anionic or potential anionic polymer) and one or more species capable of hydrogen bonding to form a starch composition, and cooking the starch composition to produce a gel.

According to this invention there is also provided a method of making a starch composition suitable for adding to a paper furnish, the method comprising cooking starch (with or without polyacrylamide) and combining the cooked starch with one or more species capable of hydrogen bonding with or without an anionic or potential anionic polymer, to form a gelled starch composition.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to solution clarification and in particular, the retention of cellulosic species, inorganic fillers, and hydrophobic suspensions such as pitch, fatty acids, sizing agents, organic fluorocarbons and other materials used in the

papermaking process. The prior art has typically centered on the addition of cationic retention aids to the papermaking furnish.

This invention relates to compositions obtained by cooking cationic or amphoteric starch with one or more anionic, cationic or amphoteric inorganic colloidal species. The starch should preferably have a degree of cationic substitution between about 0.01 to 0.30, and be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. The result of the cooking process will be a gelatinous product which may be added to a papermaking furnish as a retention aid, or used as a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer. Alternatively cationic or amphoteric starch may be cooked separately and one or more anionic, cationic or amphoteric inorganic colloidal species combined with the starch solution after the cooking process to induce gelation. The starch should preferably have a degree of cationic substitution between about 0.01 to 0.30, and be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. Combining the inorganic colloidal species and the starch solution will result in a gelatinous product which may be added to a papermaking furnish as a retention aid, or used as a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer.

This invention relates to compositions obtained by cooking cationic, anionic, non-ionic or amphoteric starch with one or more species capable of ionic or coordination bonding. The starch should be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. The result of the cooking process will be a gelatinous product which may be added to a papermaking furnish as a retention aid, or used as a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer. Alternatively cationic, anionic, non-ionic or amphoteric starch may be cooked separately and one or more species capable of ionic or coordination bonding combined with the starch

solution after the cooking process to induce gelation. The starch should be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. Combining the ionic or coordination bonding species and the starch solution will result in a gelatinous product which may be added to a papermaking furnish as a retention aid, or used a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer.

The species capable of ionic or coordination bonding may be selected from the subgroups of species containing multivalent ions, species containing multiple monovalent ions, and liganding coordination species. Such species (multivalent, monovalent and liganding coordination) may comprise or contain, but are not limited to, elements such as beryllium, magnesium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminum, boron, oxygen, sulfur, nitrogen, phosphorous, carbon and silicon containing compounds or ions, alone or in combination.

This invention relates to compositions obtained by cooking cationic, anionic, non-ionic or amphoteric starch with one or more species capable of hydrogen bonding. The starch should be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. The result of the cooking process will be a gelatinous product which may be added to a papermaking furnish as a retention aid, or used a clarifying aid for removing solids and other suspended materials from an aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer. Alternatively cationic, anionic, non-ionic or amphoteric starch may be cooked separately and one or more species capable of hydrogen bonding combined with the starch solution after the cooking process to induce gelation. The starch should be cooked at a temperature above about 60°C in an aqueous solution for a time effective to modify the starch. Combining the hydrogen bonding species and the starch solution will result in a gelatinous product which may be added to a papermaking furnish as a retention aid, or used a clarifying aid for removing solids and other suspended materials from an

aqueous dispersion. The composition may also contain polyacrylamide and/or an anionic or potential anionic polymer.

The species capable of hydrogen bonding may include but are not limited to, inorganic species such as borates, silicates, aluminates and organic species such as glycol or polyol containing moieties including oligomers and polymers such as polyvinyl alcohol, polyethylene oxide and other oligomers or polymers capable of hydrogen bonding such as polyvinyl acetate and poly(n-vinyl-2-pyrrolidinone), alone or in combination.

The cationic, anionic, amphoteric or non-ionic starch may be any of those previously used in papermaking, or other suitable starches. Cationic starch may be derived from any of the common starch producing materials such as corn starch, potato starch, tapioca starch, and wheat starch. Cationization can be achieved by any suitable procedure, such as by the addition of 3-chloro-2-hydroxypropyltrimethylammonium chloride, to obtain cationic starches with various degrees of nitrogen substitution. The degree of cationic substitution on the starches (wt. % nitrogen/starch) can range from about 0.01 to about 0.30, preferably between 0.02 and 0.15. Naturally occurring amphoteric starches, such as potato starch, or synthetic amphoteric starches, also may be selected.

It may be convenient for the cooking to be accomplished using a starch cooker at a paper mill. A batch cooker or continuous cooker, such as a jet cooker, may be selected. The solids content during cooking is preferably less than about 15%, but higher solids concentrations may be used if adequate mixing can be accomplished. Batch cooking generally is conducted at a temperature within the range of from about 60°C to about 100°C, and preferably at atmospheric pressure. Batch cooking at greater than atmospheric pressure can be practiced, thus enabling higher cooking temperatures. Continuous jet cooking typically is conducted at temperatures within the range of from about 60°C to about 130°C, and preferably at 1 atmosphere and higher pressures. Higher cooking temperatures can be used if decomposition of the starch is prevented.

Cooking time of starch or combined starch and gelation inducing species solutions should be sufficient to allow the starch to at least partially solubilize. The

selected cooking time will vary with the selected ingredients, cooking equipment and temperature, but typically will be a time within the range of from less than a second to about an hour. Longer cooking times are generally required at lower cooking temperatures.

Solution pH may be adjusted with conventional acids, bases, or salts of acids or bases, such as sulfuric acid, nitric acid, hydrochloric acid, carbon dioxide producing carbonic acid, sodium hydroxide, and potassium hydroxide. Aluminum compounds, such as alum, polyaluminum chlorides, and aluminates, such as sodium aluminate and potassium aluminate, can be used to change pH and boost retention performance.

The modified starch composition may be added to any suitable paper furnish as a retention aid to improve the retention of fines, fillers and other suspended material. The paper furnish may contain a variety of wood pulp and inorganic fillers, and typically has a pH within the range of from about 3 to about 10. Thus chemical, mechanical, chemi-mechanical and semi-chemical pulps may be used together with clays, precipitated or ground calcium carbonate, titanium dioxide, silica, talc and other inorganic fillers if desired. Such fillers typically are used at the 5 % to 30 % loading level, as a weight percent of the total paper weight, but may reach levels as high as 35%, or higher, for some specialty applications.

One particular embodiment of the invention comprises a dry starch composition suitable for forming an additive for a paper furnish. The dry starch composition includes a starch, potentially polyacrylamide and/or anionic or potential anionic polymer and species which induces gelation. The dry starch composition of the invention can be prepared, transported and stored as a dry mixture. Any suitable liquid, such as water, can be added to the dry starch composition to make a wet solution suitable for cooking and adding as an additive to a paper furnish.

Particularly advantageous results are obtained when the paper furnish also contains one or more anionic, cationic or amphoteric inorganic colloidal species. Preferably, the colloidal species is an anionic colloid. Such colloidal species may include but are not limited to montmorillonite, bentonite, titania, silica sols, aluminum modified silica sols, aluminum silicate sols, polysilicic acid, polysilicate microgels and polyaluminosilicate microgels, separately or in combination.

The dry starch composition, the wet starch composition, or the paper furnish also may contain other typical additives, such as internal sizing agents, wet and dry strength agents, biocides, aluminum compounds (such as alum, aluminates, polyaluminum chlorides, etc.), cationic polymers (retention aids and flocculants), anionic polymers, amphoteric polymers and/or separate additions of starch. Aluminum compounds in particular have been found to boost retention performance of the invention.

As mentioned above, the method of making a starch composition can be carried out by combining the starch, potentially polyacrylamide and/or an anionic or potential anionic polymer and one or more anionic, cationic or amphoteric inorganic colloidal species to make a starch composition and cooking the composition. Also, the method can be carried out by cooking a starch solution, potentially containing polyacrylamide and/or an anionic or potential anionic polymer, and combining the cooked starch solution with one or more anionic, cationic or amphoteric inorganic colloidal species to make a starch composition. Also the method can be carried out by combining the starch, potentially polyacrylamide and/or an anionic or potential anionic polymer and one or more species capable of ionic or coordination bonding to make a starch composition and cooking the composition. Also, the method can be carried out by cooking a starch solution, potentially containing polyacrylamide and/or an anionic or potential anionic polymer, and combining the cooked starch solution with one or more species capable of ionic or coordination bonding to make a starch composition. Also the method can be carried out by combining the starch, potentially polyacrylamide and/or an anionic or potential anionic polymer, and one or more species capable of hydrogen bonding to make a starch composition and cooking the composition. Also, the method can be carried out by cooking a starch solution, potentially containing polyacrylamide and/or an anionic or potential anionic polymer, combining the cooked starch solution with one or more species capable of hydrogen bonding to make a starch composition.

EXAMPLES

Ash retention trials for all of the examples, unless stated otherwise, were conducted using a simulated paper furnish comprised of 56% bleached hardwood kraft, 24% bleached softwood kraft and 20% calcium carbonate. The pulps were refined to 350 ml Canadian standard freeness. Ash retention tests were performed by using a Britt Jar equipped with a 125P screen and operated at 1250 rpm. The ash retentions were determined from the white water samples by following TAPPI Standard T-261.

Example 1

This example demonstrates how blending a cooked starch and an anionic polyacrylamide in the presence of an anionic inorganic colloidal silica together prior to the addition to the paper furnish yields better retention values than adding the three additives separately. The cationic starch (Stalok 180 from A.E. Staley) was prepared by blending 20 dry grams of starch with 1980 grams of distilled water. The blend was then cooked in a Sensors and Simulations auto-batch starch cooker with a warm up cycle of 20 minutes and a cooking cycle of 30 minutes at 96 °C. After cooking, the starch was allowed to cool to room temperature. The anionic polyacrylamide (AN 923 from SNF Floger, Inc) was prepared at 0.1 % by hydrating 1 dry gram of polymer into 999 grams of distilled water. The 0.1 % PAM solution was agitated with a magnetic stirrer for 1 hour. The colloidal silica (N-8671), a product from Ondo Nalco was prepared by mixing the equivalent of 1 dry gram of silica into 799 grams of water (0.125% solution).

A blend was prepared by first adjusting the pH of 277 grams of 1% cooked starch to 5.0 with sulfuric acid. Next, 23 grams of 0.1% PAM was added to the starch and mixed thoroughly. The pH of the mixture was then increased with sodium aluminate to a pH of 7.8. Finally, 14.7 grams of 0.125% silica was added to the starch/PAM mixture and thoroughly mixed.

For the control experiment, the starch and PAM were separately but simultaneously added to the paper furnish. The colloidal silica was added to the

furnish 10 seconds after the addition of the starch and PAM. The dosage of starch, PAM and silica were 15 lb/ton, 0.125 lb/ton and 0.1 lb/ton, respectively. The starch/PAM/silica blend was added to the paper furnish at a rate of 15 lb/ton. The ash retention results are shown below in Table 1.

Table 1

Experiment	Ash Retention
Separate Addition of Starch, PAM and Silica (Control)	49.0
Starch, PAM and Silica mixed together	56.7

The results show an increase in ash retention by mixing the starch, an anionic polymer (PAM) and an anionic colloidal species (silica) together prior to the addition to the paper furnish, in comparison with the separate addition of the additives. We would also expect an ash retention benefit by combining the starch and colloidal silica without the PAM, and if the silica was added to the starch prior to cooking.

Example 2

This example demonstrates the effects of combining a cationic starch and an anionic polyacrylamide in the presence of species capable of ionic bonding. For this example, Stalok 180 cationic starch and AN 923 anionic polyacrylamide were prepared using the same procedures as in Example 1.

For this example, three starch/PAM gels were prepared in the presence of various ionic species. The pH of the cationic starch for each gel prepared was adjusted to 5.0 with sulfuric acid prior to mixing with the anionic polyacrylamide. The first gel was prepared by thoroughly mixing 277 grams of 1% cationic starch with 23 grams of 0.1% anionic polyacrylamide. The pH of the mix was then increased to 6.5 with sodium hydroxide. The second starch/PAM gel was prepared exactly like the first blend except calcium chloride was added to the starch prior to adding the PAM. The calcium chloride was added at a ratio of 1.6:1 Ca ion: PAM. The pH of the blend

was then raised to 6.7 with sodium hydroxide. The third blend was prepared by thoroughly mixing 277 grams of cationic starch (pH 5) with 23 grams of 0.1% anionic polyacrylamide then adjusting the pH with sodium aluminate.

For the control experiment, the starch and PAM were separately but simultaneously added to the paper furnish. The dosage of starch and PAM were 15 lb/ton and 0.125 lb/ton, respectively. The starch/PAM blends were added to the paper furnish at a rate of 15 lb/ton. The ash retention results are shown below in Table 2.

Table 2.

Experiment	Ash Retention
Separate Addition of Starch and PAM (Control)	46.3
Starch and PAM mixed together made without ionic species	52.4
Starch and PAM mixed together with Ca ion present	54.1
Starch and PAM mixed together with Al ion present	58.0

The results show an increase in ash retention by the addition of the species capable of ionic bonding (Ca ion and Al ion) to the starch and PAM. We would also expect the addition of the ionic bonding species to the starch, without the PAM, to provide significantly improved ash retention compared to the starch alone. Further we would expect comparable improvement if the the species capable of ionic bonding was mixed with the starch prior to cooking.

Example 3

Example 3 demonstrates how blending a cooked starch and a species capable of hydrogen bonding together prior to the addition to the paper furnish yields better retention values than adding the additives separately. The cationic starch (S.L. 180) was prepared in the same manner as in Example 1. The polymer used capable of hydrogen bonding in this case was a polyvinylacetate (PVAC) from Rohm and Haas (Polyco 2152) which was prepared at 0.1 % by hydrating 1 dry gram of polymer into 999 grams of distilled water.

A blend was prepared by thoroughly mixing 277 grams of 1% cationic starch with 23 grams of 0.1% PVA solution.

For the control experiment, the starch and polyvinylacetate were separately but simultaneously added to the paper furnish. The dosage of starch and polyvinylacetate were 15 lb/ton and 0.125 lb/ton, respectively. The starch/PVAC blend was added to the paper furnish at a rate of 15 lb/ton. The ash retention results are shown below in Table 3.

Table 3

Experiment	Ash Retention
Separate Addition of Starch and Polyvinylacetate	45.4
Starch and Polyvinylacetate mixed together	50.4

The results show that mixing the cooked starch with a species capable of hydrogen bonding results in increased ash retention over adding the two materials separately to the paper furnish.

Example 4

This example demonstrates how cooking a blend of starch and a species capable of hydrogen bonding together prior to the addition to the paper furnish yields better retention values than adding the additives separately. The cationic starch (S.L. 180) was prepared in the same manner as in Example 1. The polymer used capable of hydrogen bonding in this case was polyvinylacetate (PVAC) from Rohm and Haas (Polyco 2152) which was prepared at 0.1 % by hydrating 1 dry gram of polymer into 999 grams of distilled water.

A blend was prepared by thoroughly mixing 20 dry grams of cationic starch with 1813.4 grams of distilled water. Next, 166.6 grams of 0.1 % PVAC was added to the starch slurry. The blend was then cooked in a Sensors and Simulations auto-batch

starch cooker with a warm up cycle of 20 minutes and a cooking cycle of 30 minutes at 96 °C. After cooking, the starch blend was allowed to cool to room temperature.

For the control experiment, the starch and polyvinylacetate were separately but simultaneously added to the paper furnish. The dosage of starch and polyvinylacetate were 15 lb/ton and 0.125 lb/ton, respectively. The starch/PVAC blend was added to the paper furnish at a rate of 15 lb/ton. The ash retention results are shown below in Table 4.

Table 4

Experiment	Ash Retention
Separate Addition of Starch and Polyvinylacetate	39.7
Starch and Polyvinylacetate cooked together	43.3

The results show that cooking the starch with a species capable of hydrogen bonding results in increased ash retention over adding the two materials separately to the paper furnish.

Ash retention trials for the following example, were conducted using a simulated paper furnish comprised of 85% Hammermill photo copy paper, 7.5% SAPPI Somerset Cover Gloss coated paper, 7.5% Tembec BCTMP, and 15% added virgin calcium carbonate. These components were blended together to obtain typical paper furnish properties such as zeta potential, filler content, conductivity, etc... often found at commercial paper mills producing alkaline wood-free coated papers.

To test the ash retention performance, a drainage/retention apparatus developed by the University of Maine was used. The procedures used were similar to those described in TAPPI standard T-261.

Example 5

Example 5 demonstrates that the ash retention performance is enhanced when a cationic starch and a polymer blend are cooked together in the presence of an aluminum compound. For this example, the anionic polymer, 7M CMC was prepared as described in the previous examples. A solution of uncooked cationic starch, Stalok 160, was made with distilled water then blended with the hydrated CMC in a dry ratio of 50:1 (starch:CMC) for a total solution solids content of 6.0% by weight. The pH of this solution was then raised to 9.0 using the aluminum compound sodium aluminate. The solution was then cooked in a jet cooker at 255 °F.

For the control experiments, the starch and CMC were separately but simultaneously added to the paper furnish at a dosage of 20 lb/ton and 0.4 lb/ton respectively. The starch/CMC blend was added to the paper furnish at a rate of 20 lb/ton. The ash retention results are shown below in Table 5.

Table 5

Experiment	Ash Retention
Separate addition of Starch and CMC (control)	53.7
Starch/CMC blend containing aluminum compound before cooking	55.5

The result shows the blend of starch and an anionic polymer, CMC, containing an aluminum compound before cooking outperformed the separate addition of starch and CMC to the paper furnish.

CLAIMS

1. A starch composition made by combining starch with a species which induces gelation, and cooking the starch before or after the combination, to produce a gel, the species which induces gelation selected from the group consisting of the following species and combinations thereof:

- (a) one or more anionic, cationic or amphoteric inorganic colloidal species;
- (b) one or more species capable of ionic or coordination bonding; and
- (c) one or more species capable of hydrogen bonding.

2. The starch composition of claim 1 in which the species which induces gelation comprises an anionic, cationic or amphoteric inorganic colloidal species selected from the group consisting of montmorillonite, bentonite, titania, silica sols, aluminum modified silica sols, aluminum silicate sols, polysilicic acid, polysilicate microgels, polyaluminosilicate microgels, and combinations thereof.

3. The starch composition of claim 1 which also contains polyacrylamide.

4. The starch composition of claim 1 which also contains a polymer bearing anionic or potential anionic groups.

5. The starch composition of claim 1 which also contains an aluminum compound.

6. A furnish including the starch composition of claim 1.

7. A furnish according to claim 6 further including an aluminum compound.

8. The starch composition of claim 1 in which the species which induces gelation comprises a species capable of ionic or coordination bonding selected from the group consisting of beryllium, magnesium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminum, boron, oxygen, sulfur, nitrogen, phosphorous, carbon, silicon containing compounds or ions, and combinations thereof.

9. The starch composition of claim 1 in which the species which induces gelation comprises a species capable of hydrogen bonding selected from the group consisting of inorganic species such as borates, silicates, aluminates and organic species such as glycol or polyol containing moieties including oligomers and polymers such as polyvinyl alcohol, polyethylene oxide and other oligomers or polymers capable of hydrogen bonding such as polyvinyl acetate and poly(n-vinyl-2-pyrrolidinone), and combinations thereof.

10. A dry starch composition suitable for forming an additive for a paper furnish, the starch composition comprising starch and a species which induces gelation selected from the group consisting of the following species and combinations thereof:

- (a) one or more anionic, cationic or amphoteric inorganic colloidal species;
- (b) one or more species capable of ionic or coordination bonding; and
- (c) one or more species capable of hydrogen bonding.

11. The starch composition of claim 10 in which the species which induces gelation comprises an anionic, cationic or amphoteric inorganic colloidal species selected from the group consisting of montmorillonite, bentonite, titania, silica sols, aluminum modified silica sols, aluminum silicate sols, polysilicic acid, polysilicate microgels, polyaluminosilicate microgels, and combinations thereof.

12. The starch composition of claim 10 which also contains polyacrylamide.

13. The starch composition of claim 10 which also contains a polymer bearing anionic or potential anionic groups.

14. The starch composition of claim 10 which also contains an aluminum compound.

15. A furnish including the starch composition of claim 10.

16. A furnish according to claim 15 further including an aluminum compound.

17. The starch composition of claim 10 in which the species which induces gelation comprises a species capable of ionic or coordination bonding selected from the group consisting of beryllium, magnesium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminum, boron, oxygen, sulfur, nitrogen, phosphorous, carbon and silicon containing compounds or ions, and combinations thereof.

18. The starch composition of claim 10 in which the species which induces gelation comprises a species capable of hydrogen bonding selected from the group consisting of inorganic species such as borates, silicates, aluminates and organic species such as glycol or polyol containing moieties including oligomers and polymers such as polyvinyl alcohol, polyethylene oxide and other oligomers or polymers capable of hydrogen bonding such as polyvinyl acetate and poly(n-vinyl-2-pyrrolidinone), and combinations thereof.

19. A method of making a starch composition, the method comprising combining starch with a species which induces gelation, and cooking the starch before or after the combination, to produce a gel, the species which induces gelation selected from the group consisting of the following species and combinations thereof:

- (a) one or more anionic, cationic or amphoteric inorganic colloidal species;
- (b) one or more species capable of ionic or coordination bonding; and
- (c) one or more species capable of hydrogen bonding.

20. The method of claim 19 in which the species which induces gelation comprises an anionic, cationic or amphoteric inorganic colloidal species selected from the group consisting of montmorillonite, bentonite, titania, silica sols, aluminum modified silica sols, aluminum silicate sols, polysilicic acid, polysilicate microgels, *polyaluminosilicate microgels*, and combinations thereof.

21. The method of claim 19 wherein polyacrylamide is also combined with the starch and the species which induces gelation.

22. The method of claim 19 wherein a polymer bearing anionic or potential anionic groups is also combined with the starch and the species which induces gelation.

23. The method of claim 19 wherein an aluminum compound is also combined with the starch and the species which induces gelation.

24. The method of claim 19 in which the species which induces gelation comprises a species capable of ionic or coordination bonding selected from the group consisting of beryllium, magnesium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminum, boron, oxygen, sulfur, nitrogen, phosphorous, carbon and silicon containing compounds or ions, and combinations thereof.

25. The method of claim 19 in which the species which induces gelation comprises a species capable of hydrogen bonding selected from the group consisting of inorganic species such as borates, silicates, aluminates and organic species such as glycol or polyol containing moieties including oligomers and polymers such as polyvinyl alcohol, polyethylene oxide and other oligomers or polymers capable of hydrogen bonding such as polyvinyl acetate and poly(n-vinyl-2-pyrrolidinone), and combinations thereof.