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(54) Titre : COMPOSITIONS D'AMIDON HYDROXYETHYLE
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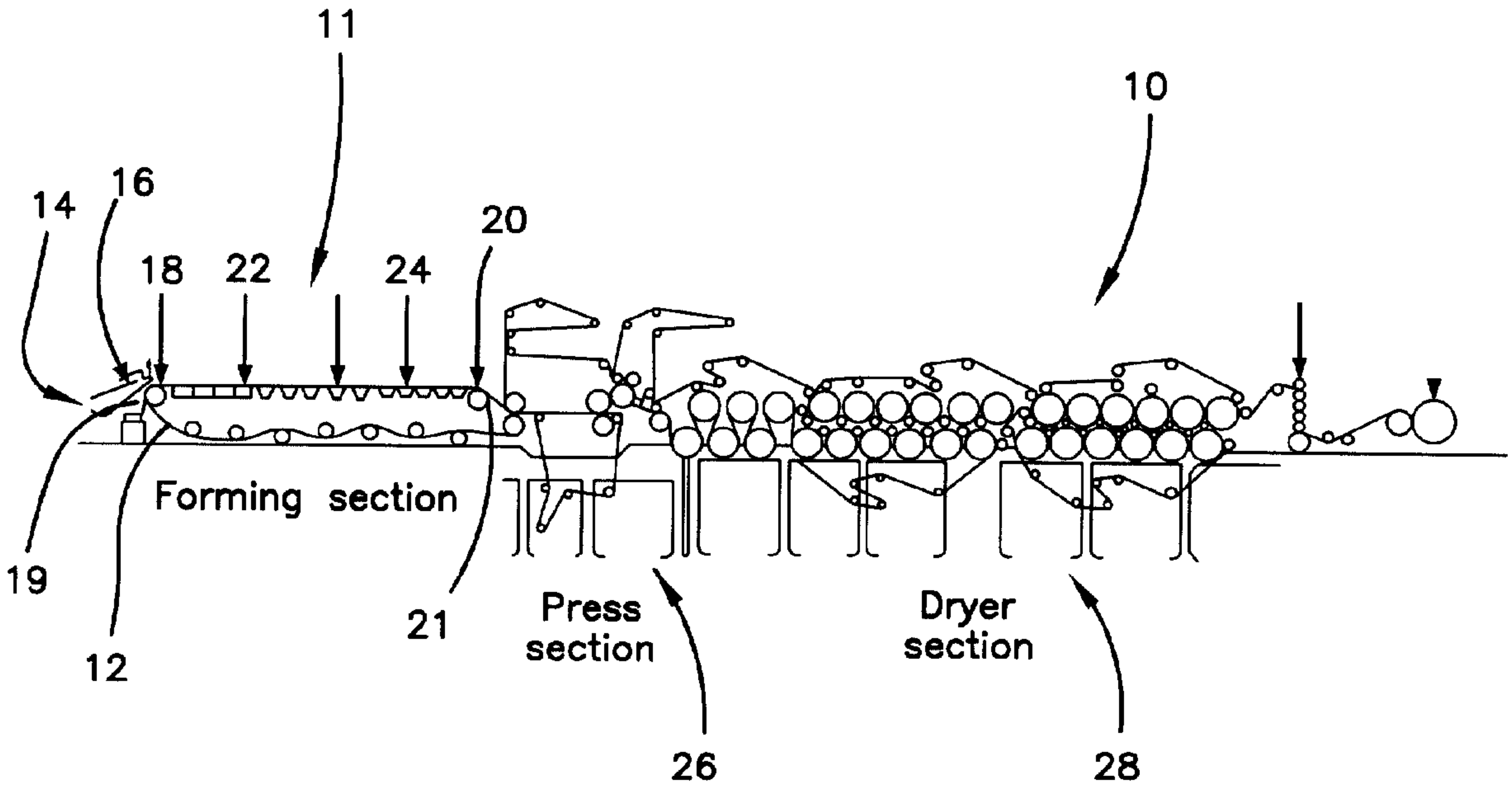


(57) Abrégé/Abstract:
A blended hydroxyethyl starch composition including dent corn starch and waxy corn starch is disclosed. The starch composition includes both amylose polymers and amylopectin polymers combined in a manner to produce a superior composition suitable for use as a surface sizing agent during the manufacture of paper products. Methods of manufacture of the composition are disclosed, including hydroxyethylation of the blended starch composition before blending the dent corn starch and waxy corn starch, as well as hydroxyethylation of the dent corn starch prior to blending with the wax corn starch. The starch composition is also suitable for incorporation in various coating compositions in addition to use as a sizing agent, such as use as a pigmented paint.

ABSTRACT

A blended hydroxyethyl starch composition including dent corn starch and waxy corn starch is disclosed. The starch composition includes both amylose polymers and amylopectin polymers combined in a manner to produce a superior composition suitable for use as a surface sizing agent during the manufacture of paper products. Methods of manufacture of the composition are disclosed, including hydroxyethylation of the blended starch composition before blending the dent corn starch and waxy corn starch, as well as hydroxyethylation of the dent corn starch prior to blending with the wax corn starch. The starch composition is also suitable for incorporation in various coating compositions in addition to use as a sizing agent, such as use as a pigmented paint.

Hydroxyethyl Starch Composition

Field of the Invention

The present invention is directed to starch compositions, methods of making and using starch compositions, and products incorporating various starches. In particular, the invention is directed to preferred starch compositions usable, for example, as sizing agents in the manufacture of paper products. The invention also concerns methods of preparing preferred compositions, methods of use, and preferred resulting products.

Background

Various paper products can be manufactured from fibers. These products are often manufactured using an aqueous slurry of fibers that includes modified cellulose fibers derived from various plant sources. Water is removed from the slurry in a controlled manner to form a web, which can be subsequently pressed and dried to form a final paper product. During manufacture, the fibers typically have hydrophilic properties to facilitate their suspension into the slurry and formation into a web.

In contrast, finished paper products preferably normally have at least some hydrophobicity to improve printability. Hydrophobicity decreases liquid (e.g. ink) absorption and enhances surface resistance to liquid penetration. Printing and writing papers often require high levels of ink holdout, resistance to wicking, and resistance to color-to-color bleed, all of which are improved by increased hydrophobicity.

Various additives can be incorporated into paper during manufacture to increase hydrophobicity. Such additives include "sizing agents" or "sizes", which are typically materials added during the wet or dry end of the papermaking process to partially seal the paper surface. Many grades of printing and writing paper are treated or sized with a surface sizing agent so that ink does not spread laterally or feather. Sizing agents can increase ink penetration time values, reduce lateral spread of printing inks, and improve imaging and contrast with various printing technologies. Some sizing agents also increase the surface integrity of sized papers, thereby often decreasing picking in uses such as printing and photocopying.

Commonly used materials for sizing agents are starches and modified starches, including oxidized, enzyme-converted, hydroxyethylated, and cationic starches. These sizing agents can have the benefit of improving strength, particularly surface strength, of the treated paper product. Traditionally, many starches incorporated into sizing agents have been composed entirely of starch derived from dent corn. Dent corn starch is relatively inexpensive compared to other starches, and has reasonably good sizing properties. Unfortunately, dent corn starch is known to retain fatty acids, which can be a problem because fatty acids interfere with the runability of the sized paper. In addition, dent corn starch is often applied to paper webs at sufficiently high loading values that the starch is a significant papermaking expense. Also, machine speeds must often be reduced in order to accommodate for the addition of the dent corn starch sizing agent.

Therefore, a need exists for an improved starch composition that may be used as a sizing agent, preferably a starch composition that has reduced fatty acid content and will allow papermakers to increase machine speeds while making stronger and lighter sheets. In addition to performing well, such starch composition should preferably be produced and applied in a cost-effective manner to provide high quality paper products.

Summary of the Invention

The present invention is directed to starch compositions, methods of making and using the starch compositions, and products made using the starch compositions. The starch compositions of the invention are particularly useful as sizing agents added to paper during dry-end processing steps.

In certain implementations, the starch composition includes a blend of 60 to 90 weight percent dent corn starch based upon total starch weight, and from 10 to 40 weight percent waxy corn starch based upon total starch weight. More preferably, the starch composition includes a blend of 70 to 80 weight percent dent corn starch based upon total starch weight; and from 20 to 30 weight percent waxy corn starch based upon total starch weight.

The starch compositions are preferably partially hydroxyethylated, such as by reaction with ethylene oxide, to add hydroxyethyl groups to the starch polymers. The weight of hydroxyethyl groups in the starch composition is preferably at least 1.0 percent, more preferably less than 1.4 percent, and even more preferably between 1.0 and 1.4 percent of the total weight of starch.

The primary starch polymers used in the starch compositions are amylose and amylopectin. The starch compositions can be manufactured by providing a starch composition containing a combination of dent corn starch and waxy corn starch. This starch composition is hydroxyethylated to produce a partially hydroxyethylated starch. Sources of starch besides dent corn and waxy corn may be used to make appropriate starch compositions. However, the starch composition should contain both amylose polymer and amylopectin polymer. The percent amylose polymer based upon total starch weight is preferably from 15 to 25

weight percent; and the percent amylopectin polymer based upon total starch weight is preferably from 75 to 85 weight percent. In particular, in a preferred implementation, the composition should contain less than 25 percent amylose polymer based upon total starch weight. Even more preferably, the starch composition contains from 18 to 22 weight percent amylose polymer based upon total starch weight; and from 78 to 82 weight percent amylopectin polymer based upon total starch weight. In an alternative implementation, a portion of the starch is initially hydroxyethylated, after which it is combined with the remaining non-hydroxyethylated starch to create a blended partially hydroxyethylated starch composition.

The hydroxyethyl starch composition of the invention may be used as a sizing agent for sizing of various webs, including wood-fiber webs such as paper and paperboard. The sized webs include a fibrous material and a sizing agent applied to the fibrous material. The improved sizing agent of the present invention results in a product having favorable sized properties. These properties can include enhanced surface strength, lower fatty acid content, and cleaner running papermaking machines. In particular, the invention can allow for equal, or better, surface strength properties of wood-fiber webs at lower starch incorporation rates than prior sizing agents, and can also create a reduction in the amount of fatty acid contaminants in the sizing agent. This reduction improves the paste clarity and cleanliness of the sizing agent. In specific implementations, the sizing agent also has advantageous rheological properties allowing for low hydroxyethyl substitution levels, good performance during application on a size press and in coating formulations, and favorable porosity and ink holdout characteristics for good printing performance.

The above summary of the present invention is not intended to describe each disclosed embodiment of the present invention. This is the purpose of the figures and the detailed description which follow.

Brief Description of the Drawing

Other aspects and advantages of the invention will become apparent upon reading the following detailed description and upon reference to the drawing in which:

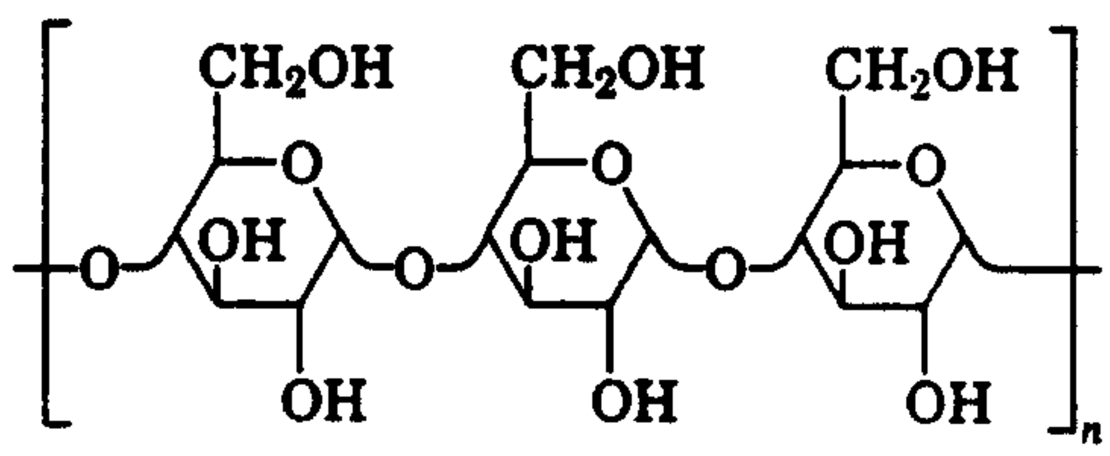
Figure 1 is a schematic view of a Fourdrinier papermaking machine, depicting the forming section, press section, and dryer section.

While the invention is susceptible to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawing and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

Detailed Description of the Invention

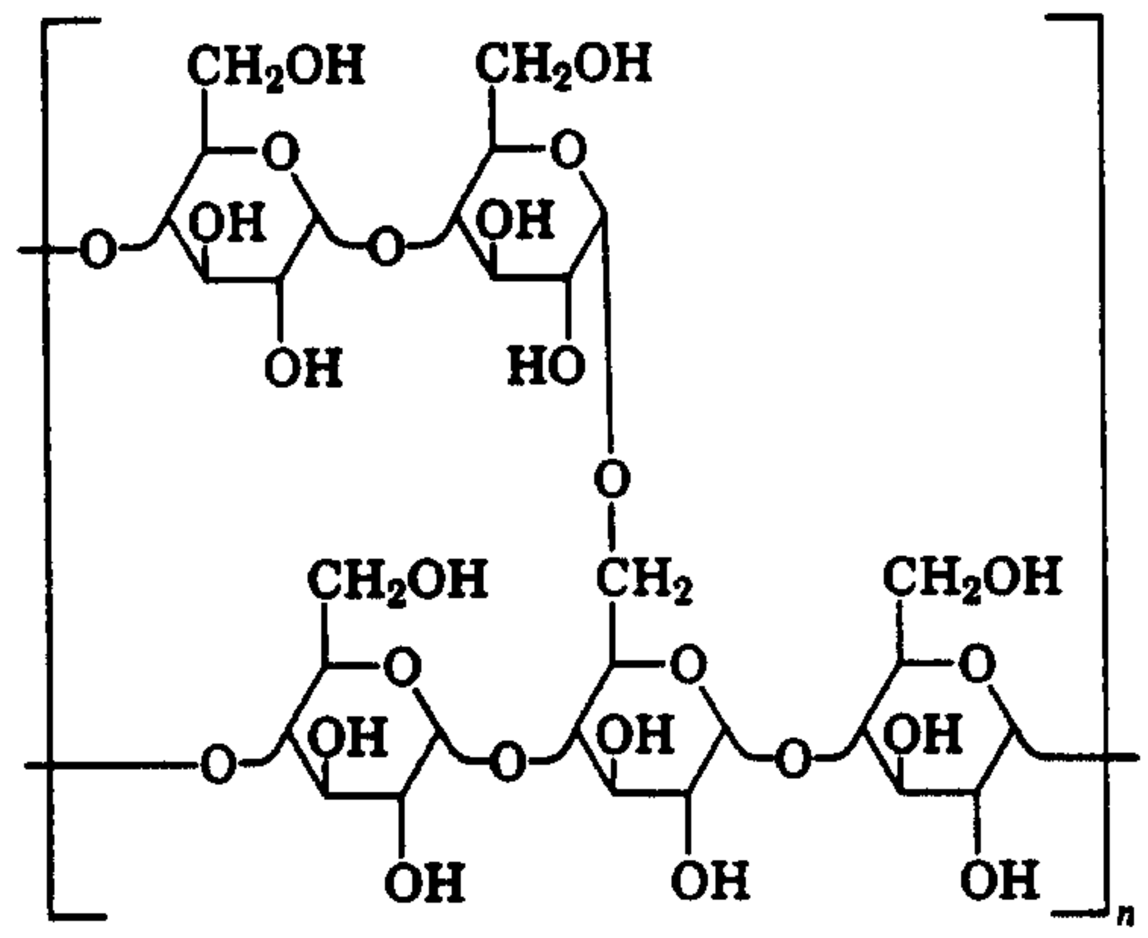
The present invention is directed to starch compositions, methods of making and using the starch compositions, and products incorporating the starch compositions. The starch compositions are preferably formed primarily of corn starch. The starch compositions of the invention are particularly useful as sizing agents added to paper during dry-end processing on a papermaking machine.

Starch is a carbohydrate polymer having glucose repeating units, and may be derived from corn, potatoes, tapioca, and other sources. As used herein, starch includes both native starch and modified starch. Modified starches include starch that has been modified, for example, by ethylation, acetylation, chlorination, acid hydrolysis, or enzymatic action. The starch compositions of the invention include both amylose polymer and amylopectin polymer. Amylose polymer is composed of repeating units of glucose connected in an *alpha*-D-(1,4) glucosidic linkage:



For amylose, the degree of polymerization (DP), which is the number of repeating glucose units, is normally in the range of 200 to 2,000. The glucose repeating units may form a 3-D helix configuration similar to what is found in proteins. This helical nature gives amylose unique binding and rheological properties, including retention of fatty acids.

The amylopectin fraction of the starch granule is composed of polymers that are much larger than the linear amylose polymers. The DP values for amylopectin range as high as 3,000,000. The amylopectin polymer achieves these values due to its branched configuration:



Amylopectin polymer forms by polymerization of the linear *alpha*-D-(1,4) fractions, during which branch points are created at the number 6 carbon atom hydroxyl group of the glucose molecule. As these branch points occur periodically along the linear chain, a large three dimensional network may develop. The branched structure of the amylopectin polymer reduces its ability to align itself with other amylose or amylopectin polymer chains, also resulting in unique rheological properties. As used herein, amylose and amylopectin include both native and modified polymers.

Amylose and amylopectin polymers form starch granules that are tightly bound together by hydrogen bonding interactions of the available hydroxyl groups on the glucose units. These hydrogen bonds make starch granules insoluble in cold water. If the water temperature is increased, the hydroxy/hydroxyl bonding gives way to hydroxyl/water interactions, and the granules may swell and hydrate. The granule swelling continues as the water temperature increases, and at some point a critical temperature is reached and the individual polymer chains are released into solution. As the amount of dissolved starch polymer increases, viscosity of the water phase increases. Shear may be introduced to accomplish complete disruption of the granule and subsequent polymer dispersion. Continued heating and shearing force the polymer chains to align themselves with the direction of the shearing action.

Three basic corn varieties are produced in the United States: yellow dent corn, waxy corn, and high amylose corn. Yellow dent corn is the most commonly produced corn, followed by waxy corn and then high amylose corn. Corn starch may be recovered from each of these varieties, using traditional corn milling methods, to form starch granules. In dent corn starch, which is starch derived from dent corn, the granule is a mixture of polymers ranging from a linear amylose fraction, to a highly branched amylopectin fraction. Percentages of each fraction in dent corn starch are approximately 27% amylose and 73% amylopectin. In high amylose corn starch, which is corn starch derived from high amylose corn, the percentage make-up is roughly reversed: 70% amylose and 30% amylopectin. Waxy corn starch, which is corn starch derived from waxy corn, has virtually no amylose and is considered to be essentially 100% amylopectin. The starch composition of the present invention includes a blend of starch containing amylose and amylopectin. The amount of amylopectin should be sufficient to provide favorable starch properties, in particular favorable sizing properties, and the starch is preferably at least 75 percent amylopectin. In certain implementations, the blend includes from 60 to 90 weight percent dent corn starch based upon total starch weight; and from 10 to 40 weight percent waxy corn starch based upon total starch weight. In a preferred implementation, the starch blend is 70 to 80 weight percent dent corn starch and 20 to 30 weight percent waxy corn starch based upon total starch weight. In another preferred implementation, the starch blend is approximately 73 to 77 weight percent dent corn starch and 23 to 27 weight percent waxy corn starch.

Although starch compositions of the present invention are preferably composed substantially of dent corn starch and waxy corn starch, other sources of starch may be used if the resulting starch composition contains both amylose and amylopectin in appropriate quantities. The percent amylose polymer based upon total starch weight should preferably be from 15 and 25 percent, and more preferably from 18 to 22 weight percent; and the percent amylopectin polymer based upon total starch weight should preferably be from 75 to 85 weight percent, and more preferably be from 78 to 82 weight percent. In particular, in a preferred implementation, the composition should contain less than 25 percent amylose polymer based upon total starch weight, and more preferably less than 22 percent weight percent amylose polymer based upon total starch weight.

The starch composition is preferably partially hydroxyethylated to add hydroxyethyl groups to the starch polymers. Hydroxyethylation results in a product having good viscosity stability and hydrolytic stability under a wide range of conditions. Hydroxyethyl starch may be produced by reacting ethylene oxide and the starch composition under alkaline conditions. The hydroxyethylation reaction is believed to proceed as hydroxide ions in the alkaline solution abstract protons from one or more of the three available hydroxyl groups on each glucose group. The starchate ions produced by the abstraction of protons attack molecules of ethylene oxide, which cause ring opening of the ethylene oxide and simultaneous production of new alkoxide ions. These alkoxide ions each pick up a proton from the water, liberating hydroxide ions for further catalysis of the reaction. The hydroxyethylation of starch is a nucleophilic reaction, and the resulting starchate ion is able to compete effectively with the relatively low concentration of hydroxide ions to give reaction efficiencies of 60 to 75%. The preparation of hydroxyethyl starch products may be done commercially on a large scale using a starch slurry produced by wet corn milling. The use of starch slurry is advantageous because the reactions can be carried out using slurry concentrations of 35 to 45%. The resulting products can subsequently be filtered, washed, and dried.

An initial step in hydroxyethylation is making the starch slurry alkaline by adding preferably 1% to 2%, based on dry starch, of an alkali or alkaline earth metal hydroxide. The starch should be kept in suspension by agitation to prevent localized pasting. Relatively high levels of caustic can be added to increase the reaction efficiency. Sodium sulfate can be added to the slurry prior to caustic addition, or it can be combined with the caustic to help prevent localized pasting during the addition.

Ethylene oxide is added to the slurry in a manner to ensure efficient solubilization, such as by use of a dip-leg. The hydroxyethylation reaction is usually conducted at 25°C to 50°C. Higher temperatures may result in swelling of the starch granules, which makes filtration difficult, while lower temperatures often require excessively long reaction times. Upon completion of the reaction, the slurry is neutralized, filtered, and washed to remove salt and soluble organic by-products.

Hydroxyethyl starch, made via the aqueous slurry reaction, is very similar in appearance to unmodified starch, but the two differ greatly in many of their other properties. The presence of hydroxyethyl groups disrupts the hydrogen bonding between starch molecules, thereby reducing the amount of energy needed to solubilize the starch in water. Thus, hydroxyethyl starch has a lower pasting temperature than unmodified starch. In addition, once solubilized, reassociation of the starch chains is inhibited. Solutions of hydroxyethyl starch have improved viscosity stability, better clarity, a reduced tendency to retrograde, and increased cohesiveness. Films are clearer and more flexible than those of unmodified starch.

Since the hydroxyethyl group is nonionic, hydroxyethyl starch does not cause flocculation of pigments or fillers. Pastes are also more stable to salts and hard water than pastes of cationic or anionic starches. The ether linkage is stable to acids and bases so that hydroxyethyl starch can be used over a wide pH range without sacrificing its desirable properties.

When starch is chemically modified, the degree of substitution (DS) is defined as the average number of hydroxyl groups derivatized per anhydroglucose unit. In the case of hydroxyethylation, the ethylene oxide can react with any of the three hydroxyl groups of the anhydroglucose unit, as well as with an already substituted hydroxyethyl group. The latter reaction results in the formation of a polyoxyethylene side chain.

The degree of substitution can be empirically determined by cleaving the hydroxyethyl group from the starch by hydrogen iodide in the presence of adipic acid and an organic solvent containing a known concentration of toluene as an internal standard. The hydroxyl groups are quantitatively converted to iodoethane, which can be detected by gas chromatography and measured relative to the area of the toluene peak. Comparison with a standard curve gives the concentration of iodoethane, which can then be used to calculate the weight percent of hydroxyethyl groups in the starch (Weight % of Hydroxyethyl Substitution). This weight percent is used to determine the degree of substitution by the following equation:

$$DS = \frac{1}{100} \times \frac{\text{Weight \% of Hydroxyethyl Substitution} \times \text{MW of Anhydroglucose}}{\text{MW of Hydroxyethyl Group}}$$

The molecular weight of anhydroglucose is 162, and the molecular weight of hydroxyethyl group is 44, so this equation simplifies to:

$$DS = \frac{1}{100} \times \frac{\text{Weight \% Hydroxyethyl Substitution x 162}}{44}$$

Using this equation, weight percent of hydroxyethyl groups is preferably less than 2.0 percent (corresponding to a DS of less than .074), more preferably less than 1.4 percent (corresponding to a DS of less than .052), and even more preferably less than 1.2 percent (corresponding to a DS of less than .044). In specific implementations, the total degree of substitution (DS) of the hydroxyl groups by the hydroxyethyl groups is preferably between .030 and .060, and more preferably between .035 and .050, and even more preferably from .042 to .048. In addition, the improved starch composition preferably contains a fatty acid concentration of less than 2.0 weight percent based upon total starch weight, and more preferably less than 1.0 weight percent based upon total starch weight.

Hydroxyethyl starch is used extensively in papermaking. The superior clarity, smoothness, and flexibility of films of hydroxyethyl starches make it especially useful for sizing paper. As used herein, the term "paper" includes a sheets, usually of vegetable fibers, laid down on a fine screen from a water suspension; as well as sheet-like masses and molded products made from fibrous cellulosic material, which may be derived from natural sources, synthetics such as polyamides, polyesters, rayon and polyacrylic resins as well as from mineral fibers such as asbestos and glass. Paperboard is also included within the broad term "paper".

Improved gloss, printability, and resistance to oily materials can result when hydroxyethyl starch is used in these applications. These properties are often essential for high-quality writing paper, magazine stock, and paper that is to be used in contact with grease or oil (e.g., butcher wrap, pastry boxes, margarine cartons). Although not approved as a direct food additive, hydroxyethyl starch is approved as an indirect food additive. It is classified as "industrial starch modifier" by the Food and Drug Administration. The viscosity stability of hydroxyethyl starch paste facilitates uniform application on the paper during coating and sizing. Hydroxyethyl starch is compatible with most components of commercially used size formulations and coating colors because of its nonionic character.

Starch sizing agents are normally applied at the dry end of papermaking machines. The most common paper making machine is the Fourdrinier machine. The Fourdrinier machine is a continuous sheet forming and drying machine used in many papermaking operations. Fourdrinier machines are common in the industry and can be used to produce virtually any grade of paper or paperboard varying from 1 to 10 meters in width and, including the press and dryer sections, may be more than 200 meters long. However, other papermaking machines, including cylinder machines, are useful in the present invention. An example Fourdrinier machine 10, shown in plan view in Figure 1, includes wet end 11 having a continuous wire screen 12 supported by various devices that improve drainage. A fiber slurry is introduced at a first end 14 of screen 12 through a headbox 16. The slurry loses water as it progresses down the wire, thereby forming the sheet.

The Fourdrinier wire screen is mounted over breast roll 18 at the intake end 19 and over couch roll 20 at the discharge end 21. Between the two rolls, the wire is supported for the most part by foils 22 and suction boxes 24. Foils 22 are elements that support the screen 12 and induce a vacuum at the downstream nip. Foil geometry can be varied to provide optimum conditions. After passing over the foils 22, the wire 18 and sheet pass over suction boxes 24, where more water is removed. After leaving the wet end 11, the sheet passes through press 26 to remove excess water, prior to the sheets entry into an evaporative dryer 28. Removal of excess water at press 26 is important for efficiency purposes because water can usually be driven out by pressing significantly less expensively than by evaporation.

Two basic characteristics of paper can be used for incorporating starch solutions into the sheet at the size press. The first is the ability of the sheet to absorb the size solution, the second is the amount of solution film passing through the nip of the size press and the manner in which the paper and roll surfaces separate. Factors that favor greater absorption include low machine speed, high sheet porosity, and lower level of internal sizing. Factors favoring greater film thickness include high sheet roughness and low nip pressure. The sheet moisture content also has a significant effect on solution pickup. Although higher sheet moisture promotes absorption, the level is typically controlled at 4 to 5% or less to ensure an even moisture profile and to keep the sizing agent nearer to the surface. Of the factors affecting pickup, solution viscosity and solids content are the most easily manipulated. The solids concentration, however, is frequently maintained at the highest manageable level consistent with the desired viscosity in order to minimize the amount of water that must be subsequently evaporated.

A relatively low-viscosity, concentrated aqueous starch solution (approximately 6 to 14 percent by weight starch to total solution weight) can be used at the size press in order to achieve starch pickup of approximately 100 lbs. per ton of product. A lower viscosity starch can be used at the calendar stack, where the pickup rate is closer to 10 lbs. per ton and a more limited penetration is desired. The sized webs of the invention include a fibrous material and a starch-based sizing agent applied to the fibrous material.

The improved sizing agent of the present invention can result in enhanced sheet strength, lower fatty acid content, cleaner running, improved rheology, and lower waste discharge and lower generation of ethylene glycol manufacturing cost relative to existing sizing agents. In particular, the invention can provide equal, or better, surface strength properties at lower starch incorporation rates than prior sizing agents, and also permit a reduction in the amount of fatty acid contaminants in the sizing agent. This reduction improves the paste clarity and cleanliness of the hydroxyethyl product in certain implementations. The sizing agent also has improved rheological properties allowing for lower hydroxyethyl substitution levels, enhanced performance on the size press and in coating formulations, and improved porosity and ink holdout characteristics for better printing performance in preferred implementations.

Heavier papers and boards may be surface-sized at the calendar stack in order to improve calendaring action and obtain a smooth, scuff-resistant surface for printing. Application of the sizing agent is usually by means of a water box with a reinforced rubber lip contacting the machine calendar roll. A sizing blade can also be used to distribute and apply the sizing agent. The sizing agent is carried on the roll surface into the calendar nip where it is applied to the board.

An additional sizing treatment can be achieved by tub sizing in which the sheet is run through a shallow bath containing a solution of starch and other additives, and excess solution is removed by passing through a light nip. Initial drying of the sized sheet is often accomplished by hot air impingement. Tub sizing is sometimes carried out on the paper machine, but can also be carried out with an off-machine operation. This treatment is utilized frequently for specialized fine papers, such as rag papers.

Machine speeds may vary chiefly based on limitations imposed by the various products produced, but also because of differences in production equipment. Heavy paperboards typically require a long drying time, and machine speeds of 50-250 m/min. are common. Very dense papers, e.g., glassine and greaseproof and condenser tissue, are difficult to dewater in the forming and press sections, and speeds range from 20 to 300 m/min are common, depending on the product. Brown grades, e.g., paper bags and linerboard, are produced at 200-1000 m/min, depending on basis weight and the site of the paper machine. Drying capacity restraints and difficulties in reeling the product limit modern tissue machine speeds to 1500 - 1800 m/min. Most tissue machines operate at lower speeds.

Almost all paper is converted by undergoing further treatment after manufacture. Among the many converting operations are coating and calendaring. The coated paper should be sufficiently smooth for printing to allow full contact between the inked image area of the plate or transfer blanket and the paper surface. Requirements for smoothness decrease from gravure printing to polymer plate to offset lithography. Printing smoothness involves not only the smoothness and compressibility of the paper, but the amount of ink, the properties or the ink-transfer and impression materials, the printing pressure, and the printing process. Consequently, smoothness is best predicted by tests that simulate the printing conditions for which the paper is intended (such as TAPPI UM466 and UM505). The starch-based sizing agent of the invention provides enhanced smoothness of the finished paper product. Comparison of ink absorbency of papers can be made according to TAPPI UM553. Bursting strength is the hydrostatic pressure required to rupture a specimen when it is tested in a specified instrument under specified conditions. It is the pressure required to produce rupture of a circular area of the paper (30.5 mm dia.) when the pressure is applied at a controlled rate according to TAPPI T403, incorporated herein by reference. In preferred implementations of the invention the burst strength of sheets of paper treated with the improved starch composition are more than 10 percent greater than materials treated with other starch compositions that are primarily or exclusively dent corn starch based.

The printing process imposes tensile stress normal to the plane of the sheet; the stress depends on the tack of the printing ink and the velocity of separation of the printing plate from the paper. The stress also tends to pick the paper, i.e., remove material, unless the paper has adequate pick strength. Papers to be printed by offset lithography require high pick strength because of the tacky inks employed, whereas gravure papers need not be so demanding. In both cases, papers to be used for multicolor printing require higher pick strengths than those used for single-color printing because of the range of tack required in the inks. To an increasing extent, pick strength is determined using printing tests that employ tack-graded inks or viscous test liquids at a controlled printing speed and pressure (see TAPPI T499 and UM507). The pick strength of a coating depends on the pigment and the type and amount of adhesive used as binders. Sheets sized with the improved starch-based sizing agent of the invention demonstrate sufficient pick strength for many traditional printing processes.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a full scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A starch composition, the composition comprising:

from 60 to 90 weight percent dent corn starch based upon total starch weight; and

from 10 to 40 weight percent waxy corn starch based upon total starch weight;

wherein a portion of at least one of the dent corn starch and the waxy corn starch is a hydroxyethyl starch.

2. The starch composition according to claim 1, wherein the composition comprises:

from 70 to 80 weight percent dent corn starch based upon total starch weight; and

from 20 to 30 weight percent waxy corn starch based upon total starch weight.

3. The starch composition according to claim 1, wherein the starch composition has a hydroxyethyl degree of substitution of .030 to .060.

4. The starch composition according to claim 1, wherein the starch composition has a hydroxyethyl degree of substitution of less .050.

5. The starch composition according to claim 1, wherein the starch composition has a fatty acid concentration of less than 1.0 weight percent based upon total starch weight.

6. A starch composition, the composition comprising:

15 to 25 weight percent amylose polymer based upon total starch weight; and

75 to 85 weight percent amylopectin polymer based upon total starch weight;

wherein at least a portion of the amylopectin polymer has been hydroxyethylated.

7. The starch composition according to claim 6, wherein the composition comprises at least 18 to 22 weight percent amylose polymer based upon total starch weight; and 78 to 82 weight percent amylopectin polymer based upon total starch weight

8. The starch composition according to claim 6, wherein the starch composition has a hydroxyethyl degree of substitution of at least 1 percent.

9. The starch composition according to claim 6, wherein the starch composition has a hydroxyethyl degree of substitution of .030 to .060.

10. The starch composition according to claim 6, wherein the starch composition has a hydroxyethyl degree of substitution of less than .050.

11. The starch composition according to claim 6, wherein the composition has a fatty acid concentration of less than 1.0 weight percent based upon total starch weight.

12. A paper product, the paper product comprising:

a fibrous web;

a starch-based agent on the fibrous web, the starch-based agent resulting from applying a starch-based sizing agent comprising a starch composition containing 15 to 25 weight percent amylose polymer based upon total starch weight, and 75 to 85 weight percent amylopectin polymer based upon total starch weight;

wherein a portion of at least one of the amylose polymer or amylopectin polymer is a hydroxyethyl polymer.

13. The paper product according to claim 12, wherein the starch-based sizing agent has a hydroxyethyl degree of substitution of less than .050.

14. The paper product according to claim 12, wherein the starch-based sizing agent has a fatty acid concentration of less than 1.0 weight percent based upon total starch weight of the starch composition.

15. The paper product according to claim 12, wherein a first sheet of the fibrous web from claim 12 containing the starch-based agent of claim 12 has a burst strength at least 10 percent greater than the burst strength of a second sheet of the same fibrous web sized with a starch-based sizing agent in which at least 27 percent of the starch is amylose polymer, wherein the same amount of a starch-based sizing agent and the same sizing method are used to size the first sheet and second sheet.

16. The paper product according to claim 15, wherein the burst strength is measured according to TAPPI method T403.

17. A paper product, the paper product comprising:

a fibrous web;

a starch-based agent on the fibrous web, the starch-based agent resulting from applying a starch-based sizing agent comprising a starch composition containing 60 to 90 weight percent dent corn starch based upon total starch weight, and 10 to 40 weight percent waxy corn starch based upon total starch weight;

wherein a portion of at least one of the dent corn starch or waxy corn starch is a hydroxyethyl starch.

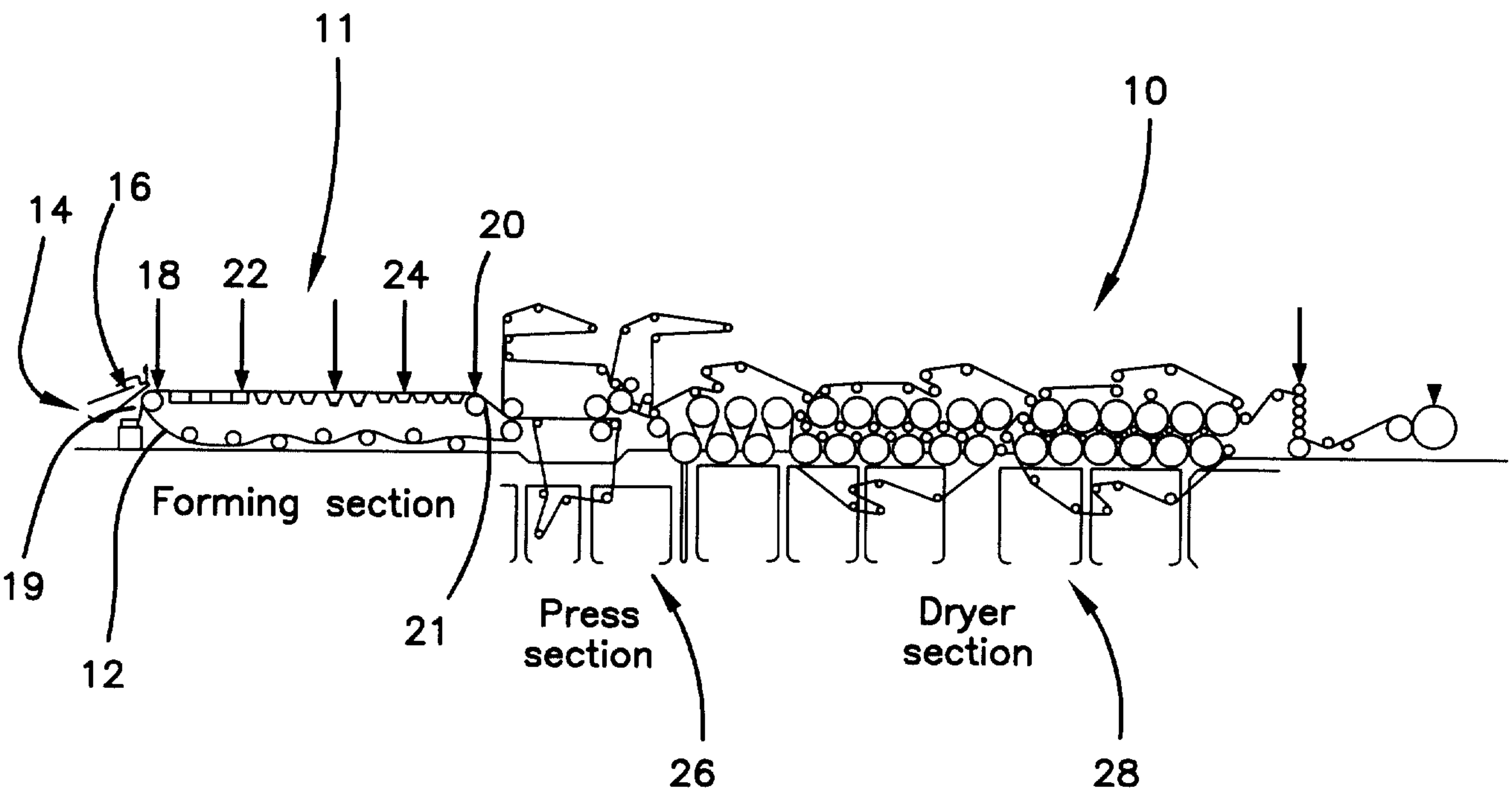
18. The paper product according to claim 17, wherein the starch-based sizing agent has a hydroxyethyl degree of substitution of less than .050.

19. The paper product according to claim 17, wherein the starch-based sizing agent has a fatty acid concentration of less than 1.0 weight percent based upon total starch weight of the starch composition.

20. The paper product according to claim 17, wherein a first sheet of the fibrous web from claim 17 containing the starch-based agent of claim 17 has a burst strength at least 10 percent greater than the burst strength of a second sheet of the same fibrous web sized with a starch-based sizing agent in which at least 90 percent of the starch is dent corn starch, wherein the same amount of a starch-based sizing agent and the same sizing method are used to size the first sheet and second sheet.

21. The paper product according to claim 20, wherein the burst strength is measured according to TAPPI method T403.

FIG. 1



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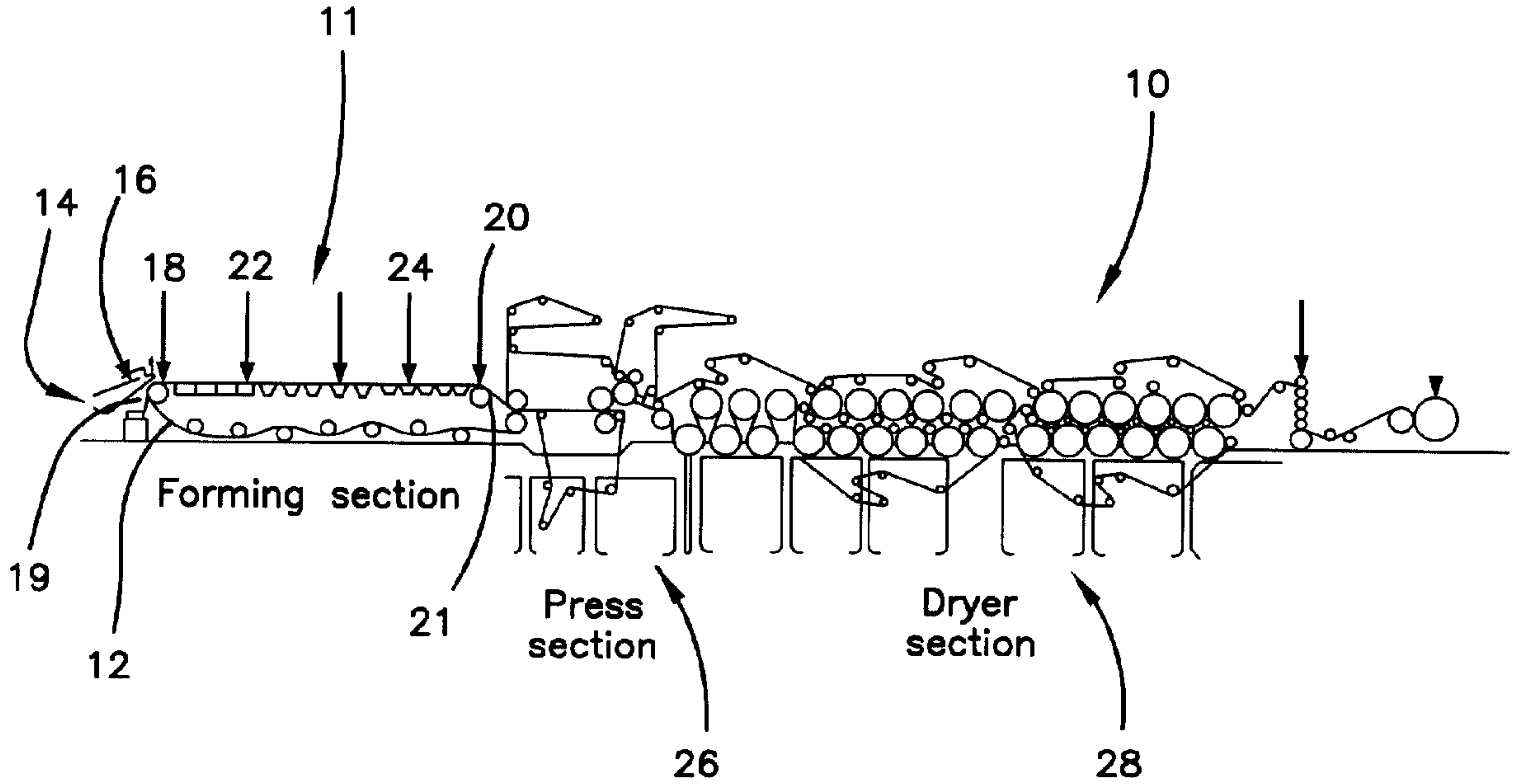

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