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Size Press Practices and Formulations Affecting Paper Properties and Process Efficiency: A Review

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Size presses on paper machines are used to apply a solution of a polymer – usually starch – to the surface of the sheet and thereby to increase the stiffness, surface strength, and printing quality of the product. This article reviews publications dealing with the size press equipment, the materials, and factors affecting both the operating efficiency and attributes of the resulting paper. The emergence of film-press equipment (*e.g.* blade-metering size presses) in the 1980s has greatly decreased the frequency of web breaks and increased productivity. Starch technology at the size press, though relatively mature, continues to evolve. By adjustment of starch attributes, solids levels, and incorporating other additives, modern papermakers can tune size press outcomes to meet a range of paper product requirements, including strength, hydrophobicity, and the reduction of air permeability. By application of various synthetic polymers, mineral particles, and even nanocellulose in combination with starch or other base polymers, there is potential to extend the technology to meet a range of future needs for paper products.

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Contents:

INTRODUCTION

This article reviews published information about size press practices, including the equipment, procedures, materials, operating efficiency, and effects on paper properties. The main goals of running a size press on a paper machine include increasing paper's stiffness and surface strength. The resulting paper is usually less dusty, such that it can be printed with less contamination of printing presses. Such attributes mostly can be attributed to three main categories of factors, which will be considered in this review, namely the size press equipment, the applied materials, which traditionally have been forms of starch, and various procedural options.

The scope of this article can be defined, first of all, by describing how a size press differs from a conventional aqueous coating operation used in the manufacture of paper. Both operations apply aqueous formulations continuously to the surface or surfaces of a web of paper. A key difference is that the solids content (as the sum of dissolved and any insoluble components) is much lower in the case of size presses, which typically are run in a range of 5 to 18% of soluble polymeric matter (Klass 1998). By contrast, typical water-based coating formulations often have a total solids content in the range of 30 to 65% (Klass 1998). The major component of a typical coating formulation is insoluble pigment, *e.g.* clay or calcium carbonate. Although some papermakers apply mineral pigment at a size press, the major polymeric component usually still is dissolved starch. Another distinguishing feature is that a size press operation takes place during passage of the sheet between a pair of cylindrical rolls, whereas most coating operations involve a blade or some other device to remove an excess of applied material.

Unlike typical coatings on paper, a typical size press application is not expected to result in a continuous film (Cushing 1979). Due to the relatively high amount of water present in the formulation, there would not be sufficient material to completely fill the void spaces in the paper. Pan *et al.* (1995) developed a way to predict the progressive emptying of pores and deposition of material during the drying of paper coatings, and this mechanism seems to be appropriate for the situation being considered here.

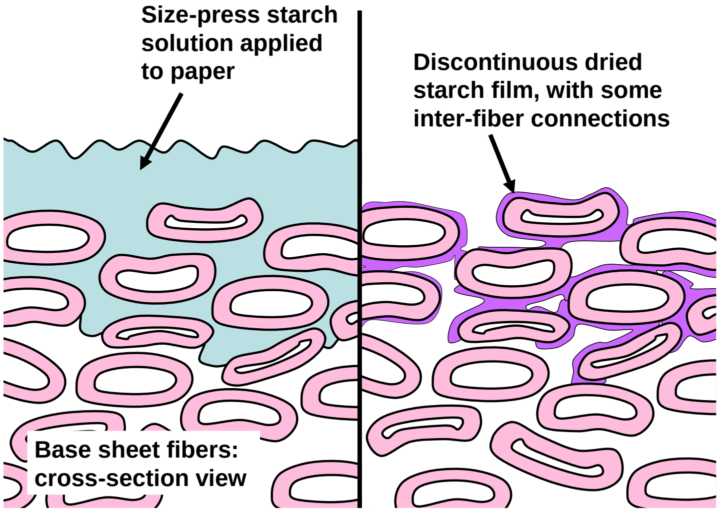


Fig. 1. Depiction of expected main locations of the size press formulation before and after drying, such that the solids end up spread one the fiber surfaces and collected at junctions between fibers

Figure 1, which is based on the cited work, illustrates a hypothetical process by which evaporative drying after a typical size press can be expected to promote accumulation of starch and other size press components at or near to the junctions between fibers within the paper sheet, as well as on the outer surfaces of the fibers. In this figure the fibers are depicted in cross-sectional view, such that their central lumen spaces can be seen. Readers seeking information about aqueous coating technologies for paper are recommended to study appropriate parts of the textbook by Paltakari (2009).

Though many of the articles to be cited in this document show clear improvements in paper properties resulting from size press applications, it is important to keep in mind that any rewetting of a paper sheet can negatively affect the inherent properties of the base sheet. This was shown most clearly by Lepoutre *et al.* (1986), who applied water to the paper surface as one of their control conditions. The strength and other properties of those water-sized sheets were always inferior to those of the basestock. The effect was attributed to the swelling and debonding of the paper web. In addition, there is no wet-pressing operation after a size press.

Another way to define the scope of this article is to consider where the size press fits into the overall process of manufacturing a hypothetical paper product. The size press is almost always an "on-machine" unit operation, meaning that it operates in a continuous mode together with the paper forming device and associating paper drying equipment. Thus, the paper sheet entering the size press has just been formed, pressed, and then dried for the first time by passage around a series of steam-heated dryer cans (Smook 2016). Since the paper becomes wetted by the starch (or other) solution applied at the size press, it subsequently needs to be dried again, almost always by means of a further series of dryer cans. Typically, about 1/3 of the drying capacity on a paper machine comes after the size press (Eklund 1989). Depending on paper property requirements, the surface-sized paper could then be coated or subjected to various converting operations.

A key potential advantage provided by a size-press operation is the fact that nearly 100% of the added material goes directly onto or into the paper product (Helle 1971; Hoyland *et al.* 1977; Gray and Rende 2005; Hemmes and Wahl 2017). This is in contrast to the wet end of a paper machine, where certain components that are small or lacking in strong binding to the fiber surfaces may require multiple passes through the forming device before they are retained, and some may pass into the wastewater. An inherent disadvantage of size press usage is the fact that the paper needs to be dried twice. Adding a size-press operation to a paper machine will always increase the steam requirement. The increased drying requirement is likely to impose a further restriction on the speed of production. Another inherent issue concerning size-press application is that the distribution of the solution on the paper surface can be non-uniform. The uniformity of the applied size-press formulation also can be affected by base-sheet uniformity. The splitting of the starch film as the sheet exits the nip tends to produce an "orange peel" effect, the subtle nature of which often allows that effect to escape notice. However, when a dye or whitening agent is being applied onto to the surface, such effects can become apparent under appropriate lighting.

Fluorescent whitening agents (FWAs) provide a good example to illustrate the differing priorities when deciding to add something at the wet end of a paper machine, the size press, or both. At the wet end, where the priority is on achieving high retention onto the fiber surface, papermakers mainly employ tetrasulfonated FWAs (which are often the cheapest) or disulfonated FWAs (which are the least soluble and therefore the easiest to retain) (Sampl *et al.* 2021). By contrast, papermakers often employ hexasulfonated FWAs at the size press; they are the most water-soluble, which allows the material to diffuse and move throughout the sheet to some extent after application. The goal is to achieve a more uniform optical effect, especially when viewing under ultraviolet light.

After the main sections covering literature related to size press equipment and size press additives, some other emerging trends and opportunities will be reviewed, based on more recent publications. For instance, so-called "pigmented size press" operations have become much more attractive following developments in the design of size press equipment (which is the next topic). It has been proposed by some writers that by adding certain process chemicals at the size press, the wet-end chemical operations can be simplified (Brouwer 1997; Hemmers and Wahl 2017). In addition, the concept of adding nanocellulose at the size press offers some possibilities and challenges. Nanocellulose tends to increase the viscosity of a mixture, and excessively high viscosity can place a limit on the speed of running a size press. Finally, there is increasing interest in applying eco-friendly barrier materials at the surface of paper, so there will be strong interest in how size-press applications might contribute to such product goals.

It is important to acknowledge the existence of earlier review articles, without which the present article would have been much more difficult to complete. Some important sources are listed in Table 1.

Table 1. Review Articles, Books, and Chapters about Size Presses, the Applied Materials, and their Results

Topic of Review Article, Chapter, or Book	**Reference**
Surface sizing, with broad coverage of traditional technologies	Cushing 1979
Surface applications to paper, including size presses and coating	Eklund 1989
Size press technology trends and developments	Klass 1990a
Surface sizing: notes from a TAPPI short course	Latta 1997
Starch separation from its sources and its industrial uses	Ellis *et al.* 1998
Metering size press development, from a historical perspective	Klass 1998
Film press usage for pigment application to paper	Zou & Vidal 2003
Interactions between a coating or size press film and the base-stock	Engström 2005
Textbook covering both coating and size press issues	Paltakari 2009
Starch-based materials for biodegradable packaging	Tian & Jin 2021
Corn starch technology, including industrial applications	Yu & Moon 2022

EQUIPMENT

Three classes of equipment that can play critical roles in a size press operation are the size press itself, the run tank that supplies the formulation, and optional drying equipment, such as any non-contact drying devices. In addition, there are some important options to consider with respect to the devices used to prepare starch solutions.

Size Press Configurations

The most important distinction between different categories of size press devices has been between the traditional "flooded nip" size presses and the so-called "film presses" (Eklund 1989; Felder 1991; Kohl *et al.* 1999). In addition, certain types of coater devices sometimes have been employed in lieu of size presses to apply starch to paper, especially before the emergence of film presses (Fineman and Hoc 1978a,b; Klass 1988; Bailey 1996).

Typical size press equipment, including both flooded nip and film press varieties, involve passage of the paper web between two press rolls. In flooded nip (or "pond") size presses, typically at least one of the rolls is "soft," meaning that it is covered with a rubber or polyurethane layer (Moore 1998), and the other can be "hard," *i.e.* a steel roll (Eklund 1989). Gray and Rende (2005) indicated that hardness values in the range of 20 to 30 P & J (measured with a Pusey & Jones Plastometer) are common. In principle, the compliance of the roll cover facilitates a more even pressure across the width of a paper machine. Coyle (1988) calculated the degree to which a soft roll surface can be expected to deform in the course of applying a fluid material to a non-porous web. The corresponding situation in which the fluid is able to penetrate into the web was considered by Ninness *et al.* (2000). Devisetti and Bousfield (2010) measured the pressure distributions when using porous paper webs with applications of fluids with press nips. Differential equations were developed to describe the deformation of the soft roll covers and the effects of such variables as fluid viscosity and speed.

Flooded nip size presses

In a flooded nip or "pond" type of size press, the paper is exposed to a pool of aqueous solution before entering the nip between two rolls. The press nip itself contributes to the role of metering the applied amount. As shown in Fig. 2, three main types of flooded nip size presses can be identified by the relative positions of the two press rolls, *i.e.* vertical, inclined, and horizontal (Eklund 1989; Smook 2016). From an idealized perspective, the horizontal format would seem ideal, since it would facilitate keeping equal conditions of wetting of the paper in the ponds on each side of the sheet. But the inclined format is most popular, probably because it is more consistent with the main direction of travel of the sheet from the wet end towards the dry end of the paper machine, and possibility minimizing the required space.

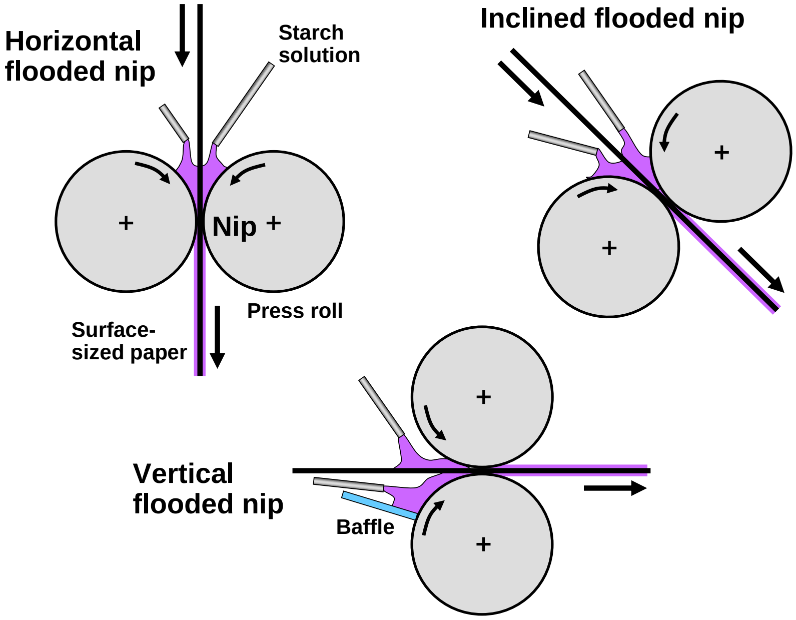


Fig. 2. Schematic depictions of three basic layouts of flooded nip size press that were in common usage before the general transition to film press systems

Before the introduction of film presses, one of the best options for starch application onto a paper web may have been the Billblade® coater, which is sketched in Fig. 3 (Hansson and Klass 1984; Klass 1988). Work by Fineman and Hoc (1978a,b) showed that such a coater could be used to upgrade the quality of printing papers. For instance, it was possible to reduce linting problems in offset printing presses. The linting problems were further reduced by use of a hydrophobic agent in the size press formulation.

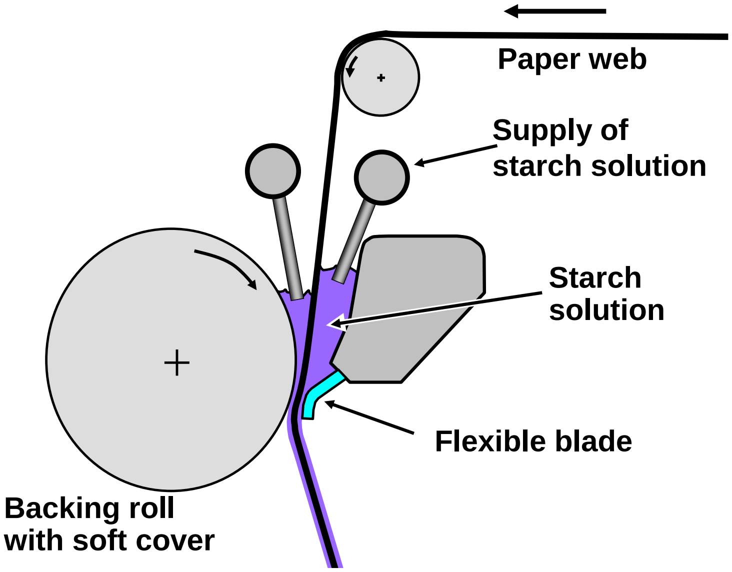


Fig. 3. Schematic diagram of a Billblade® system, which was formerly sometimes used for starch application to paper

An inherent problem with flooded nip size press installations has been a relatively high frequency of sheet breaks. Such problems may become more serious with increasing web speed, which has been attributed to flow instabilities and splashing in the ponds (Linnonmaa and Trefz 2009). Exposing a paper sheet to a pool of relatively hot liquid incurs risk that the paper web will become wetted all the way to its core, thereby reducing its strength so much that the web breaks. Though such effects can be countered by hydrophobic sizing treatments during formation of the base-sheet, such internal sizing can raise the cost of production, and the web may still break due to defects. If the hydrophobicity or other properties of the paper are not equal across the width of the paper machine, the size press solution uptake may be non-uniform, which can lead to paper quality problems.

Although flooded nip size presses are still employed on some older and smaller paper machines, such practices are becoming less common. However, the distinction between flooded nip size presses and more recent generations of equipment needs to be kept in mind when reading literature about size press operations in general. As will be shown in subsequent sections, some operating variables that tend to be critical for flooded nip presses may be inconsequential for some other size press operations.

Pre-metered film presses

A film press can be defined as a type of size press in which the starch (or other) solution is first applied to one or both of the press rolls as a film, such that there is essentially no "pond" as the web passes through the nip. The rolls no longer have the function of metering the amount applied to the paper. Rather, the uptake is determined by (a) the amount of film applied to the roll, (b) the permeation into the sheet mainly due to the applied pressure in the nip (Eklund 1989), and (c) the splitting of the film that remains in mobilized form between the paper and the adjacent roll at the exit from the nip (Dobbs 1993). Because film presses, in general, do not wet the paper before it is actually passing through the nip, the possibility of complete wetting of the sheet is essentially eliminated, and this translates in a greatly decreased probability of size-press breaks of the web (Hiorns and Sharma 1996; Lipponen *et al.* 2004). A further contribution to this goal is provided by the fact that film press systems often allow for increases in starch solids (Lipponen *et al.* 2004). A higher solids level of the applied starch means less water to evaporate, in addition to a higher viscosity, such that the starch layer remains more towards the surface and the first layers of fibers in the sheet (Bergh and Hemmes 1991). Table 2 highlights articles focusing on a variety of aspects related to film-press operations and outcomes.

Table 2. Film Press Equipment and its Usage

Highlights of Article	Citations
Depth of penetration of starch applied by the film press	Bergh *et al.* 1988
Specialty paper grade development using the film press	Bergh & Svenka 1990
The use of a film press to achieve high operating speeds	Seebass 1992
Comparison of various film press technologies	Tehomaa *et al.* 1992
Use of a grooved rod in a film press design	Rantanen & Finch 1994
Wood-free and wood containing grades using film presses	Akesson 1996
Pilot plant equipment for testing of film press formulations	Bailey 1996
Paper grade enhancements made possible by film presses	Aarnikoivu 1998
Historical development of film presses in the early 1980s	Klass 1998
Theory and practices of film press technology	Knappich 1998
Troubleshooting rheology problems in film presses	Triantafillopoulos & Smith 1998
Ongoing displacement of flooded nip by film-press devices	Kohl *et al.* 1999
One-sided film-press applications for specialty paper grades	Arnold *et al.* 2000
Use of a film press as a precoat before conventional coating	Kaipf *et al.* 2000
Structure of mineral coating layer formation with a film press	Forsström *et al.* 2003
Use of film presses for application of pigmented coatings	Zou & Vidal 2003
Film press starch solids levels and rheological issues	Lipponen *et al.* 2004

Typical wetting times of the incoming sheet before the size press nip can be roughly estimated based on the process speed and the observed length of contact with any pond or contact with a film before the press nip. Note that a slower speed should be assumed in the case of a flooded nip size press, since it is unlikely that such equipment would currently be used on faster paper machines. Based on these rough estimates, there may be a ten-fold difference in pre-wetting time, if not more (Table 3).

Table 3. Estimates of Time of Wetting before the Nip, Depending on Wetted Length before the Nip and Operating Speed

Size Press Type	Assumed speed of paper machine (m/min)	Assumed wetted length before nip (mm)	Time of wetting before the nip (sec)
Flooded nip	1000	150	9 ms
Film press	1000	15	0.9 ms
Film press	2000	15	0.45 ms

Metering blade film presses

The general features of a metering blade size press are shown in simple form in Fig. 4, Part A. As shown in Part B, the applicator system is likely to be a type of "short dwell" coating system (Triantafillopoulos and Aidun 1990; Gray and Rende 2005), using equipment that is essentially the same as is commonly used for some pigmented coating operations directly onto paper. Short-dwell devices act like a nozzle, such that there is no contact between air and the starch solution before the spreading of the film. Regardless of how the film is spread, the application is made onto the surface of a relatively large rubber-covered roll (Eklund 1989). This type of device is well suited for the application of a starch film onto paper intended for printing purposes. According to Rantanen and Finch (1994), blade-metering presses also can be used for pigmented coatings, up to a medium level of solids.

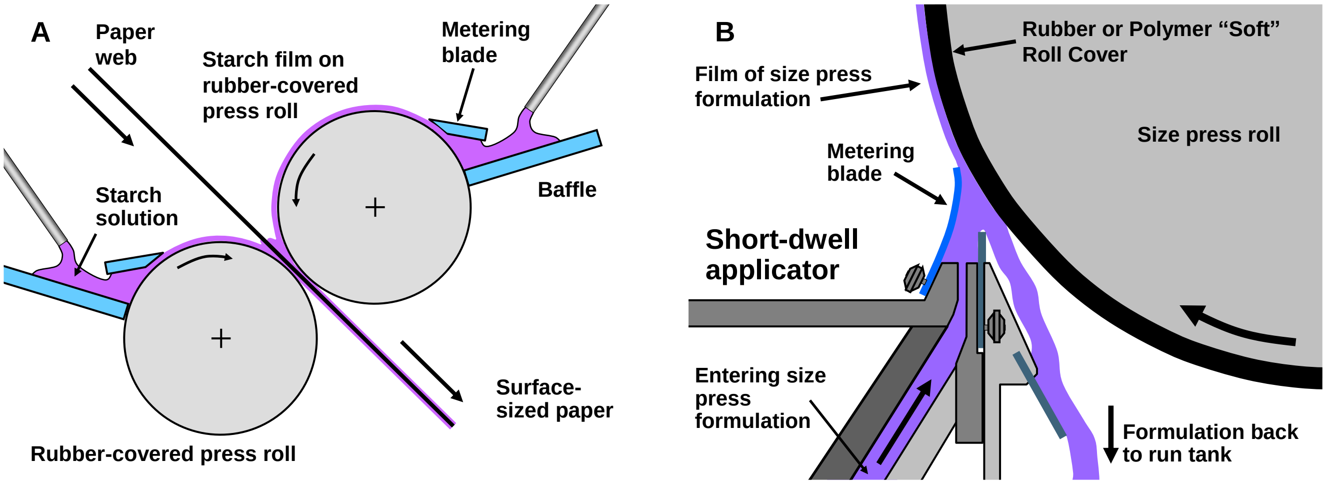


Fig. 4. Schematic diagram of a blade-metering size press system. A: Basic layout; B: Option with a short-dwell applicator. The drawing of the short-dwell system was inspired by a similar drawing in Gray and Rende (2005).

Metering rod film presses

Metering rod systems are similar to what has been just described, except that the amount of size press formulation spread as a film is governed by what can pass through the openings between a wire-wound rod at the roll surface (Poranen and Kataja 2000). To change the amount applied, one can change either the solids concentration or replace the rod with one that has a different size of wound wire. Though the film applied to the roll may retain a fine streaky appearance, corresponding to the wrapped wires, the idea is that such features will become irrelevant as the film passes through the nip and gets partly squeezed into the paper surface. With respect mineral coatings, Rantanen and Finch (1994) recommend using groove roll applicators for film presses only for low-solids applications.

An alternative to the grooved rod is the smooth rod (Roper *et al.* 2022). The cited authors used such a device for the application of barrier coatings onto paper. When using a smooth rod, the amount of formulation applied to the press roll can be decreased by increasing the pressure, decreasing the diameter of the rod, or by decreasing the solids content of the formulation (Linnonmaa and Trefz 2009).

Gate-roll size press application

As a historical precursor to the modern film press, it is also possible to prepare a starch film or coating film on a transfer roll by means of a gate-roll application. This scenario is sketched in Fig. 5. As in the size press configuration depicted in Fig. 4, the gate role can be classified as a pre-metered system. Wilson (2005) reported that Beloit developed such a system in which only the two central press rolls rotated to match the velocity as the paper web. The next outer rolls rotated at 50 to 90% of the sheet velocity, and the outermost rolls rotated at 20 to 50% of the velocity at the outsides of the rolls. According to Klass (1998), gate-roll coaters were introduced in the 1960s, but they tended to suffer from short roll cover lifetime, problems due to film splitting, and limitations with respect to coating rheology. Linnonmaa and Trefz (2009) give 800 m/min as an upper limit for the speed during effective gate-roll usage for film press applications.

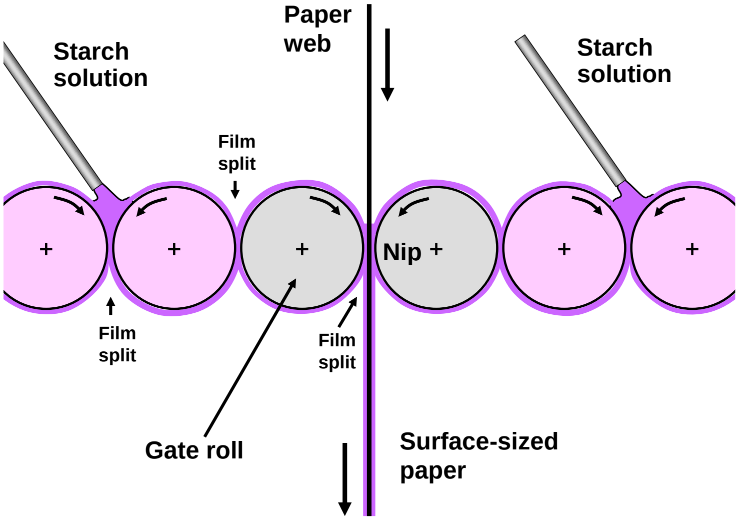


Fig. 5. Schematic diagram of a gate roll size press system

Jet applicators for the film press

As a more recent modification, jet applicators have been developed to gain better control and cleanliness during as a size press formulation is transported to the point of application onto the size press rolls (Kaipf *et al.* 2000). Rather than using a blade or rod, the formulation is applied by means of non-contacting multi-jet nozzles to the size press roll surfaces. Temperatures and flow rates are controlled. One of the reported benefits of this technology is decreased debris transferred to the surface of the first drying cylinder following the film press.

Coaters for starch application

Pigmented size-press formulations often have been used to precoat the paper sheet ahead of a final coating operation (Paltakari and Lehtinen 2009). Balzereit *et al.* (1995) ran trials and showed that a metering size press could be used to apply an initial pigmented coating (*i.e.* pre-coating) before a final blade coating. According to Bailey (1996) such applications can be expected to be used as pre-coatings, not for replacement of existing blade coating operations for existing grades of paper.

Run Tank for the Size Press

Before a starch solution is sent to the size press, it is usual that it to be held in a run tank (Walter 1998). This is where conditions such as temperature, formulation viscosity, pH, and other quantities can be monitored and sometimes controlled. Mixing within the run tank can ensure complete uniformity of the incoming starch solution with other additives, such as hydrophobic copolymers, colorants, fluorescent whiteners, defoamers, *etc.* (Paltakari and Lehtinen 2009). If there is any return flow from the size press (as is common for flooded nip presses), it will be a continuous input to the run tank too. Features of the run tank system can include level control, heating (sometimes by a steam jacket), solids or viscosity monitoring, and the filtering of the formulation. To minimize problems, a first priority is to avoid splashing and entrainment of air in the starch circulation system, especially in the path back to the run tank (Wilson 2005). Walter (1998) discusses how careful design of the run tank and related equipment can minimize the entrainment of air and the production of foam.

Dryer Adaptations for the Size Press

When applying starch solutions to the paper surface, it is typical to feed the outgoing damp web into a conventional dryer section, composed of steam-heated steel cylinders (Smook 2016). As was noted earlier, the proportion of "after-dryer" cans may be about 1/3 of the total on the whole paper machine (Eklund 1989), though that proportion might be subject to a decrease with an increase in solids level of the size press formulations. In principle, if there is a lot of wet solution at the paper surface, then there is a greater likelihood of starch deposition onto dryer cans; thus, conditions that favor more penetration of size-press formulation into the paper tend to reduce deposits on dryer can surfaces (Wilson 2005).

Other drying devices may be needed, at least initially, in cases where the size press formulation is tacky, as when latex products are in the formulation. In such cases it may be necessary to employ air-turns, infrared drying, or combinations of different non-contact drying technologies, at least initially (Rennes 1998a,b). For instance, Turunen (1996) recommended that non-contact drying be considered when running pigmented coatings at a size press. In addition, the multi-jet applicator system for film presses has been reported to result in less contamination of conventional after-drying operations.

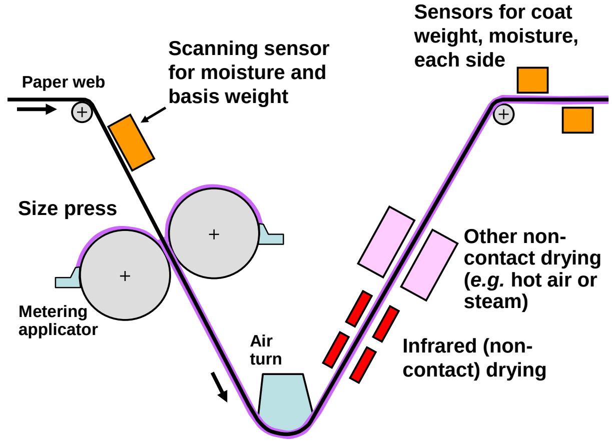


Fig. 6. Possible positioning of online sensors to permit automatic control of drying operations associated with a size press (redrawn based on an original by Shapiro, 1998)

When preparing a range of paper products, with the use of a size press, there can be increased importance of maintaining tight control of operations. Shapiro (1998) showed that such control can be facilitated by use of certain online sensors. These can include sensors for temperature and percent solids. In addition, the pick-up amount can be controlled. A further step is to use a camera to detect possible defects after the operations. The likely positions of some of these sensors, related to drying of the web after a size press, are illustrated in Fig. 6.

CHEMICAL ADDITIVES AT THE SIZE PRESS

Overview of Size Press Additives

Because starch plays such a large role in most size press operations (Cushing 1979), this section will first consider its main chemical properties, its most important sources, from the standpoint of papermaking, how it is separated from other components of the plant source, and how it is prepared for use at the size press. Other options include polyvinyl alcohol (PVOH) (Kane 1978; Lertsutthiwong *et al.* 2004; Kim *et al.* 2017; Bhardwaj and Bhardwaj 2018; Abhari *et al.* 2018a,b; Liu *et al.* 2021) and carboxymethyl cellulose (CMC) (Paltakari and Lehtinen 2009). Optional additives include hydrophobic agents, colorants, and fluorescent whiteners.

Starch Fundamental Properties

Chemistry

Regardless of the plant source, starch can be described as a polysaccharide composed exclusively of anhydroglucose subunits (Ogunsona *et al.* 2018; Cheng *et al.* 2021). Unlike cellulose, the anhydroglucose units are connected by the alpha rather than the beta form of glycosidic bonds, which leads to very different behavior. As shown in Fig. 7, there are two co-existing forms of starch that are present in most, but not all starchy plant materials (Bergh and Hemmes 1991).

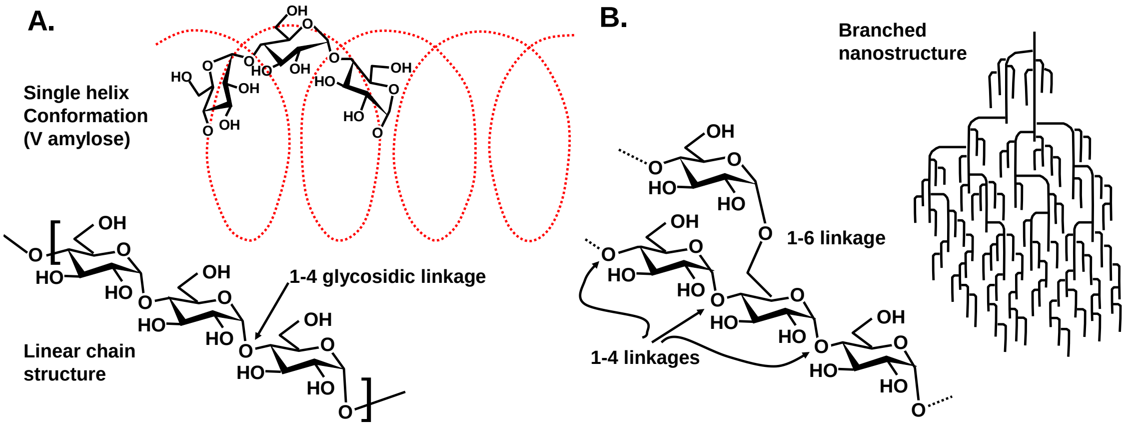


Fig. 7. Two forms of starch macromolecules that coexist in most starchy plant materials.
A: Amylose, showing the linear chain structure and the native V helical conformation;
B: Amylopectin, showing the branched chain structure and linkage details

The simpler of the two is amylose, which is comprised of linear chains in which alpha glycosidic linkages connect the C1 of one unit to the C4 of the next. Depending on the plant source, the amylose often has a degree of polymerization of about 800 to 3000 (*ca.* 130,00 to 500,000 g/mole) (Ellis *et al.* 1998). The more complex form is amylopectin, in which approximately 4% of the anhydroglucose units provide a branch point, and these are associated mainly with its C6 hydroxyl group (Thompson 2000). The linear segments are typically about 10 to 12 anhydroglucose units in length. The high level of branching within amylopectin gives rise to relatively dense, compact molecular having a degree of polymerization of about 20,000 (*i.e.* molecular weights of about 300 million g/mole) (Willett *et al.* 1997).

Conformation

An amylose molecule, when it has been dissolved in water, adopts various helical conformations (Imberty *et al.* 1991; Gessler *et al.* 1999; Tan *et al.* 2007; Putseys *et al.* 2010). The amylose chains may be present either as double helices (A- and B-type amylose) or as a helix formed from a single chain (V-amylose). The amylose components of native cereal starch, such as corn starch, tend to be dominated by A-amylose, whereas native tuber starch, including potato starch, tends to have more B-amylose (Imberty *et al.* 1991). The cited authors described how A-amylose can be converted to B-amylose.

The single-chain V-type helices have a central cavity that is relatively hydrophobic (Immel and Lichtenthaler 2000). The orientation of the –OH groups of the coils are such that they mainly render the outsides of the coils hydrophilic, whereas polar groups are absent from the insides of the helices. As a consequence, any hydrophobic components of the material, such as fatty acid monomers, are likely to be contained as inclusion compounds within the V coils (Yan *et al.* 2012). The cited study showed that palmitic and stearic acid could be included in size press formulations by this means, thus contributing to the hydrophobicity of a resulting linerboard product. It appears that the proportion of V-amylose increases in proportion to the amount of oleophilic monomers present (Cheetham and Tao 1998). X-ray crystallography has shown evidence of increasing V-amylose content in the crystalline phase with increasing proportions of amylose (Tan *et al.* 2007). However, in the cited work, double-helix forms of amylose tended to be dominant.

Crystallinity

Within the plant, the amylose molecules are likely to be associated in a relatively loose crystalline arrangement of adjacent V-type coils (Immel and Lichtenthaler 2000; Conde-Petit *et al.* 2006) or double-helix coils. Amylopectin molecules, despite their complex structures, also have been reported to adopt a regular arrangement when present in plant materials (O'Sullivan and Perez 1999; Genkina *et al.* 2007). Though present together, the amylose and amylopectin may be present in different micro-domains within a starch grain.

Changes in crystal form

The state of crystallinity changes when starch is cooked, which is sometimes called a pasting operation (Wang *et al.* 2015b; Wani *et al.* 2016; Reyniers *et al.* 2020). The amylose form of starch generally shows the most significant effects of retrogradation (Miles *et al.* 1985; Fredriksson *et al.* 1998). Initially, the cooking appears to solubilize some of the amylose as intact V helices, as already described (Immel and Lichtenthaler 2000; Conde-Petit *et al.* 2006). In the case of amylopectin, the solubilized starch solutions appear to be amorphous and not readily subject to further formation of regular structures. Solubilized amylose from corn gradually adopts a double-helix form (A-helices) that can self-associate into undesirable structures, and these can separate from the solution (Conde-Petit *et al.* 2006; Fang *et al.* 2020). This process is called retrogradation or "set-back" by papermakers, and it generally hurts the ability of the starch to act as a bonding agent within paper (Liu *et al.* 2007). In general, retrogradation can be limited by applying the starch solution to paper soon after the starch has been prepared. In particular, long storage or gradual cooling of the starch solution is to be avoided (Cushing 1979). Walter suggests adjusting the temperature of cooked starch to no higher than 72 °C but no lower than 60 °C to minimize retrogradation. Retrogradation is also promoted by low pH and the presence of multivalent metal cations such as calcium or aluminum (Cushing 1979). Figure 8 illustrates one likely route of transformation among different helical forms of starch and their semi-crystalline agglomerated forms. Though amylopectin is generally not noted for a high level of retrogradation, Fechner *et al.* (2005) reported its conformational changes occurring relatively quickly after a pregelatinization process, by means of Raman spectroscopy. Blennow *et al.* (2001) showed that amylopectin can undergo agglomeration, leading to multi-chain structures, as quantified by gel permeation chromatography. Miles *et al.* (1985) described such changes to cooked amylopectin as being "reversible".

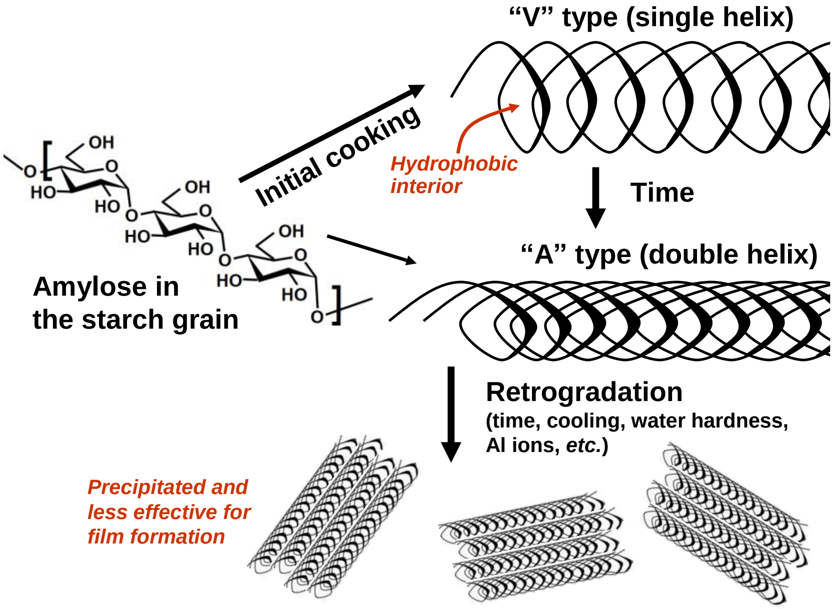


Fig. 8. Simplified portrayal of changes in amylose starch conformation and colloidal form starting with the natural form present in the grain, then cooking, conversion to a different helical form, and finally retrogradation, which appears to involve aggregation of the A type of amylose helices

Starch Source Materials and Starch Isolation

Especially from a North American papermaking perspective, the most important plant sources of starch products are maize (corn) varieties, though potato starch is also widely used. Tapioca and wheat starches are also used, depending on the location (Ellis *et al.* 1998). Typical starch grain shapes and sizes are illustrated in Fig. 9 (Alvarez-Ramirez *et al.* 2019). In the cited work, the corn starch grains had a mean longest dimension of 12.2 µm, while the corresponding value for potato was 41.2 µm. In each case, it was determined that the grains swelled by only about 7% when immersed in room-temperature water for 8 hours.

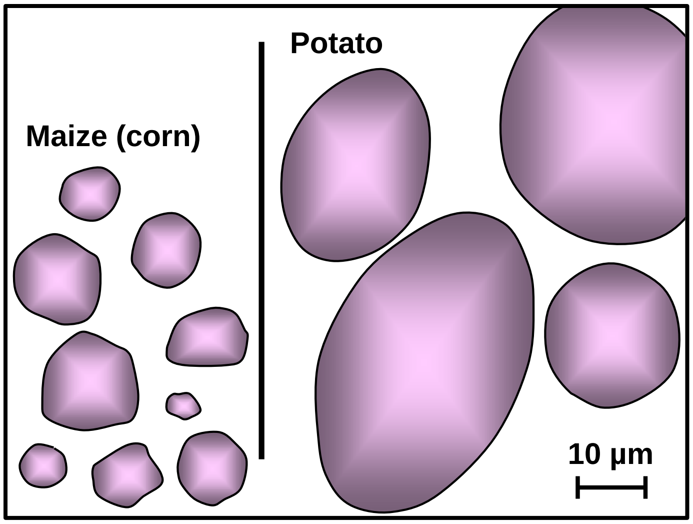


Fig. 9. Basic starch grain sizes and shapes illustrated for two starch types commonly used in papermaking applications (traced from micrographs of Alvarez-Ramírez *et al.* 2019)

Corn starch and its isolation

The maize (corn) variety most often used as a source of starch for papermaking is *Zea maize* L., which has been called dent corn. This is the same species that is used for corn sweetener and other food uses; therefore, it has a huge volume of worldwide production. The mean diameter of grains is about 15 µm (Ellis *et al.* 1998), and the particles can be described as spheroidal, but not smooth. The term "polyhedral" has also been used (El Halal *et al.* 2019; Reyniers *et al.* 2020). The lipid content in a grain of corn starch is relatively high, about 0.6%, as is the level of protein (0.35%) (Ellis *et al.* 1998). The amylopectin level is about 72% of the starch, with amylose accounts for the remaining starch. The amylose in corn has an average degree of polymerization of about 800 (Ellis *et al.* 1998) or about 960 to 990 (Reyniers *et al.* 2020). Because its molecular mass is relatively low, compared to some other forms of starch, the amylose present in dent corn is more susceptible to retrogradation. This is consistent with the opaque nature of pastes and films prepared from dent corn starch, as would be expected from the inclusion of crystalline particles in the micrometer size range. The gelatinization temperature of dent corn starch is about 75 to 80 °C (Ellis *et al.* 1998).

Waxy maize is a hybrid form of starch that is grown exclusively for non-food applications, such as papermaking. Because it contains near to zero amylose, it is almost free from the effects of retrogradation after it is cooked. The lipid content (about 0.15%) is lower than that of dent corn. The starch grains are generally similar to those of dent corn, though the pasting temperature can be somewhat lower (65 to 70 °C rather than 75 to 80 °C) (Ellis *et al.* 1998).

To isolate maize starch, the grain is first soaked (steeped) in dilute sulfurous acid for one to two days (Yu and Moon 2022). The corn oil is extracted, and then the starch is separated from the gluten and fiber components following a wet-milling operation. Since wet-milling tends to release sulfur from the protein component, 1-cyseine can be added in an acidic medium as a reducing agent to release the starch from its protein binder in the grain (El Halal *et al.* 2019). These authors also described an alternative separation process starting with the steeping of corn kernels in 0.1% sodium bisulfite solution for about a day at 50 °C, followed by drainage and wet-crushing, filtration (100-mesh, then 270-mesh), decantation and removal of the supernatant, and then separation of the starch solids by centrifugation.

Potato starch and its isolation

Potato starch can be obtained from purpose-grown potatoes or as a byproduct from potato processing into such products as potato chips or French fries. Of the starch products used for papermaking, potato starch has the largest grain size (averaging about 30 µm diameter) and having a "fat oval" shape (Ellis *et al.* 1998; Reyniers *et al.* 2020). Potato starch typically has lower levels of lipids and proteins compared to maize, but it contains phosphorous (about 0.08%, dry mass basis), which gives it a weak anionic charge. The typical degree of polymerization of the amylose component in potato starch is about 3000, which is much higher than the other forms of starch (Ellis *et al.* 1998). This difference is expected to render the material somewhat slower to retrograde in comparison to maize and some other starches. Also, the pasting temperature (60 to 65 °C) is somewhat lower than the other forms of starch used by papermakers (Ellis *et al.* 1998).

Tapioca starch

Tapioca has similarities to maize starch, including its typical grain size, but its lipid and protein contents are lower, each at about 0.1% (Ellis *et al.* 1998). The degree of polymerization of its amylose component is relatively high, similar to that of potato starch, and its amylose content is relatively low, about 17% (Ellis *et al.* 1998).

Wheat starch

Wheat starch, in comparison to the types described above, tends to have relatively small grains (average diameter 10 µm) and relatively high levels of substances that might be regarded as impurities, *i.e.* 0.8% of lipids, 0.4% of proteins, and 0.06% of phosphorus (Ellis *et al.* 1998). The amylose content is as high as that of corn starch (28%), and the degree of polymerization of the amylose is also relatively low (about 800) (Ellis *et al.* 1998).

Starch Modification

For reasons of efficiency and economy, chemical modifications of starch are often carried out before the starch is either cooked (gelatinized) or converted (reduced in molecular mass). For that reason, it makes sense to describe the chemical modification steps first, even though they are optional, from the perspective of size-press practices. Chemical modifications can substantially raise the cost of starch production, and since the amount of starch applied at the size press can be relatively high (*e.g.*, 5% of the mass of a typical printing paper sheet), there is a strong incentive to use underivatized starch, which is often called "pearl starch." Some of the important chemically modified forms of starch are oxidized, cationic, and hydroxyethyl.

Oxidized starch

Oxidized starch products are widely used at the size press (Craig *et al.* 1968; Cushing 1979; Dobbs 1993). By reaction with sodium hypochlorite, some of the hydroxyl groups are converted to carboxylic acid groups, which contribute a negative charge to the starch when it its cooked. More detail related to oxidized starch is given later in the context of viscosity reduction, *i.e.* starch conversion.

Hydroxyethylated starch

One of the most widely used starch derivatives for size-press usage is the non-ionic product hydroxyethylated starch (Banks *et al.* 1973). This starch derivative is known for providing tough films. Though the derivatization necessarily adds to the cost of production, the resulting non-regularity of the product's molecular structure renders it highly resistant to retrogradation (Ellis *et al.* 1998). The hydroxyethylated starch also has been reported to stay out near to the surface of paper (Cushing 1979). Such behavior is likely due to a reported tendency for transient self-association among the chains (Jauregui *et al.* 1995). Figure 10 shows the basic structure of hydroxyethylated starch. The relative frequency of substitution onto -OH groups in different positions within the starch molecular structure was studied by Merkus *et al.* (1977).

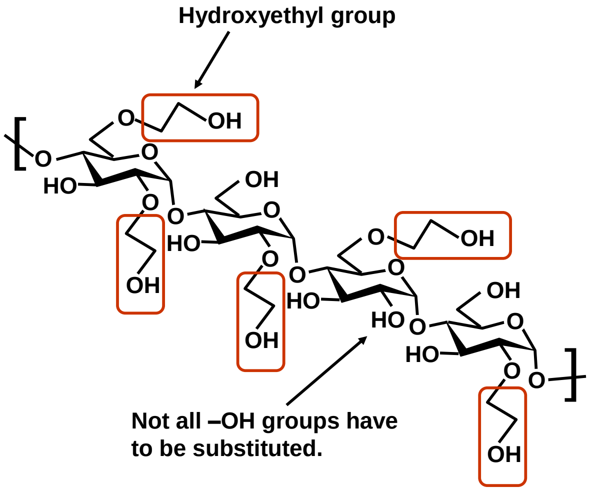


Fig. 10. Hydroxyethylated starch molecular structure

Cationic starch

Derivatization of starch with amine groups provides a positive ionic charge to the macromolecules when the starch is later dissolved. Though this can be considered almost an essential requirement for starch being added at the wet end of a paper machine (Harvey *et al.* 1979; Roberts *et al.* 1987), there are reasons for some papermakers to prefer cationic starch products also for size press addition. For one thing, if some defective paper needs to be repulped and formed again into paper (*i.e.* it is repulped), the cationic size press starch component will tend to be efficiently retained on the negatively charged surfaces of cellulosic fibers (Rankin *et al.* 1975; Cushing 1979; Hamerstrand *et al.* 1979; Ellis *et al.* 1998; Lee *et al.* 2002). In addition, it has been reported that cationic size press starch products have a greater tendency to stay out near to the surface of paper, thus providing more surface strength and stiffness to the product (Cushing 1979; Lee *et al.* 2002; Andersson and Järnström 2006). Though such effects might be attributed to electrostatic attraction of the cationic starch to negatively charged carboxylate groups at the fiber surfaces, it is also likely that differences in rheological properties are involved. Wilson (2005) mentions that early attempts in the 1950s to add cationic starch at the size press were unsuccessful, and it had been suggested that the problems were due to the electrostatic interactions with the fiber surfaces.

To prepare cationic starch, the suspension of starch grains is treated under highly alkaline conditions with epoxypropyl-trimethylammonium chloride or a related compound (Bergh and Hemmes 1991; Butrim *et al.* 2011). Subsequent cooking of such starch yields molecular chains that have an affinity for cellulosic surfaces.

Cyclodextrin

An innovative technology has been demonstrated by which natural oils, or other hydrophobic monomeric compounds, can be incorporated into a specialty paper product, possibly allowing their gradual release over time (Aguado *et al.* 2022). This was achieved by crosslinking of the starch with cyclodextrin, taking advantage of the hydrophobic character of the interior of that ring-like saccharide. Note that this effect is mechanistically related to the hydrophobic nature of the interiors of V-type amylose helices, as described earlier (Immel and Lichtenthaler 2000).

Pregelatinization

For some specialty applications of size press starch, there may be an advantage of using a starch product that does not require cooking at the point of usage. Such advantages can be achieved by a process called pregelatinization (Alexander 1995; Liu *et al.* 2017). Briefly stated, a slurry of starch grains is heated to an optimized extent, then dried before storage and shipping. Alternatively, extrusion may be used as a means of achieving the same effects (Liu *et al.* 2017). Though pregelatinization does not immediately solubilize the grains, it renders them susceptible to subsequent swelling and solubilization when the redried grains are placed in warm water.

Starch Conversion

Solutions of native starch, at the concentrations that papermakers would prefer to employ them, generally have too high a viscosity to be able to pass correctly through a size press nip or through under the blades or rods used for applying the starch film to a film-press roll. Excessively high starch viscosity can cause “nip rejection,” which may manifest itself as unstable operation of the size press (Abell and Knowles 2001). In some cases, jets of starch solution are emitted from the pond area, possibly spattering the paper web (Wilson 2005). Thus, one of the first steps, carried out either at the starch company or in the paper mill, is to reduce the degree of polymerization to an optimum range suitable for the local equipment and the grade of paper being made. Conversion can be accomplished by use of enzymes, oxidizing agents, or ultrasonic treatments, as will be described below (Brenner *et al.* 2016).

Enzymatic conversion

When enzyme conversion of size-press starch came into use (Hughes and Craig 1950), it was viewed as an advantage, since it avoided the use of oxidizing agents (see later) (Bajpai 2018). According to Wang *et al.* (2022), enzyme-converted size press starch often achieves superior results compared to other forms of converted starches. The conversion is carried out with α-amylase, which is usually obtained from *Bacillus subtilis*. However, Wang *et al.* (2022) found advantages of using some different types of α-amylase to prepare size-press starch, possibly giving a better contribution to paper strength at a given level of viscosity. Conditions such as temperature and treatment time before usage need to be optimized, depending on the targets for viscosity and solids content (Li *et al.* 2013). The authors just cited suggest treatment at 65 °C for 20 minutes at 20% solids, with

0.02% enzyme dosage, a $CaCl_2$ concentration of 0.04%, and pH near to 6. After the conversion, the starch needs to be cooked (see later) (Cushing 1979; Li *et al.* 2013; Wang *et al.* 2022). The overall procedure is shown schematically in Fig. 11. As an alternative, Cave and Adams (1968) describe a fully continuous process that can include both enzyme conversion and the cooking of starch.

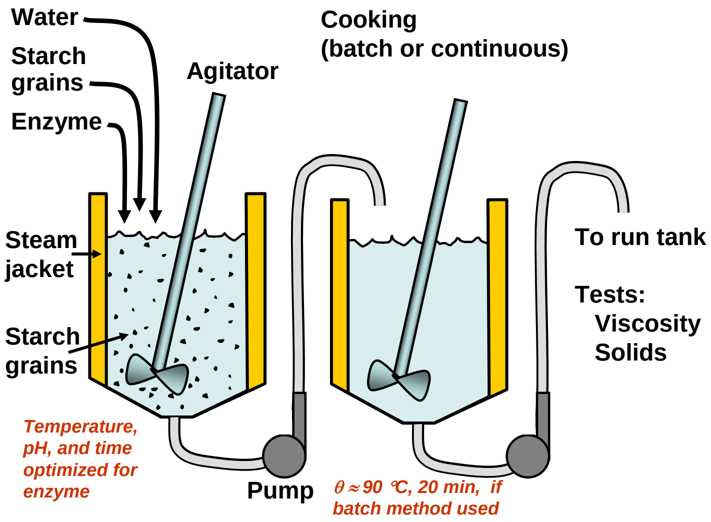


Fig. 11. Steps in enzyme conversion of starch to decrease its degree of polymerization and viscosity at a given solid level. The term θ here refers to temperature.

Ammonium persulfate conversion

In-mill preparation of size-press starch is often conducted by treatment of the grain slurry with ammonium persulfate (Craig *et al.* 1968; Dobbs 1993). In addition to decreasing the degree of polymerization, the oxidation also induces an anionic charge to the starch, in its wet forms.

Hypochlorite oxidization conversion

Especially when the molecular mass is to be reduced before size-press starch is shipped to the paper mill, a preferred method is oxidation, by means of hypochlorite (Cushing 1979). When such treatment involves heating, it can be called thermo-oxidative degradation (Brogly 1978; Brenner *et al.* 2016).

Ultrasonic conversion

As a means to avoid possible toxic byproducts, another alternative to hypochlorite oxidation involves ultrasonic treatment (Brenner *et al.* 2016; Radosta *et al.* 2016). Such treatment was shown to cleave the amylopectin component, breaking off the branch points, while leaving the linear amylose chains relatively intact. Such a process would be expected to generate undesirable very-low-mass fragments. At a given viscosity, the starch tended to have higher penetration into the sheet (Brenner *et al.* 2016).

Optimized molecular mass

A topic that often gets lost in discussion of conversion of size-press starch is the fact that there is always a relationship between molecular mass and the ability of a starch product to contribute to paper strength. The effect may be negligible at relatively high molecular mass, but the effects can become large when the degree of conversion reaches excessive levels, which need to be determined by experimentation. Thus, Brandl (1984) found that excessively high temperatures during continuous cooking of starch decreased the viscosity excessively, resulting in over-usage of starch at the size press. Dobbs *et al.* (1993) documented a case study in which a paper mill was able to save money by backing off on the level of enzyme treatment, thus increasing the degree of polymerization of the resulting starch. Although the resulting higher viscosity meant that the operators had to reduce the solids of the size-press solution, they were still able to achieve their target paper strength levels.

Starch Cooking

There are two main ways to cook or "gelatinize" the starch grains (Leach 1965; Ai and Jane 2015), often just before their usage in papermaking. The most traditional method is a batch process, whereas most modern operations have adopted continuous or "jet" cooking procedures.

Batch cooking

Batch preparation of starch generally takes place in steam-heated vessels, as has been illustrated in Fig. 11. To ensure even mixing of the starch granules, the initial mixing with water is carried out below the softening point for the given starch product. Then the temperature is raised to the neighborhood of 90 °C and held for up to about 20 minutes, depending on the starch product. During this period, the starch granules start to swell. With continued swelling, they will become more translucent, and then starch macromolecules will start to be released. Especially when cooking potato starch, the viscosity of the mixture will go through a maximum (Leach 1965; Swinkels 1985), which is likely due to friction between a crowded population of over-swollen grains. Once the starch has been fully cooked, the structural contribution to viscosity is no longer present and viscosity reaches a plateau that depends on molecular mass and solids content. In the case of converted starch products, the viscosity levels will be much lower than the native starches, often by one or two factors of ten.

Continuous (jet) cooking

Continuous cooking of starch offers the potential advantages of smaller equipment (no need for steam-heated tanks), better opportunities for process control, and less opportunity for the build-up of dried starch at waterlines (Hiemstra 1972). On the other hand, good process control is required, with respect to temperature and pressure, to ensure optimal results (Herwig 1979). As illustrated in Fig. 12, cooking takes place under pressure within what might best be described as an enlarged pipe, following a valve in which steam is introduced to heat up the mixture. The solids content fed to the jet cooker needs to take into account the final solids target (*e.g.* maybe 10 to 18% in different cases), as well as any dilution needed cool the mixture to reach a target run temperature (*e.g.* 65 or 70 °C). Jet cooking temperatures in the range 100 to 140 °C can be used (Fanta *et al.* 1999; Byars 2003; Ferng *et al.* 2011). The time of treatment is often hard to define, due to the possibility of continued cooking after the cooked starch is diluted and released from the pressurized zone. Bradl (1984) showed that factors such as temperature and pressure need to be carefully controlled at optimum values to achieve consistently favorable results with a jet cooking system. In particular, under-cooked starch may result if the supply of steam has variable properties.

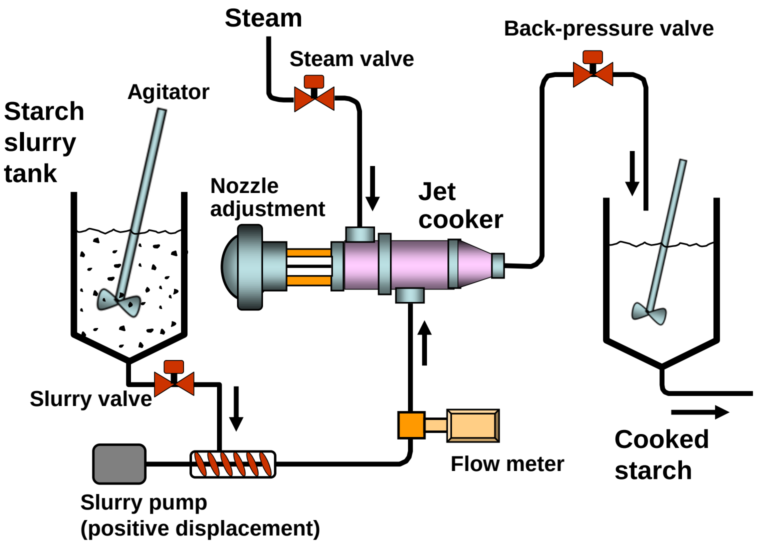


Fig. 12. Schematic illustration of a jet cooking process for continuous, rapid cooking of a starch grain suspension

Viscosity monitoring

Key variables, from the point of view of process control, include starch solids and viscosity. Solids content is conveniently monitored by checking the refractive index of the solution. Viscosity measurements are often done with devices that essentially measure drainage time through an orifice (Monteiro *et al.* 2023). These tests are illustrated in Fig. 13.

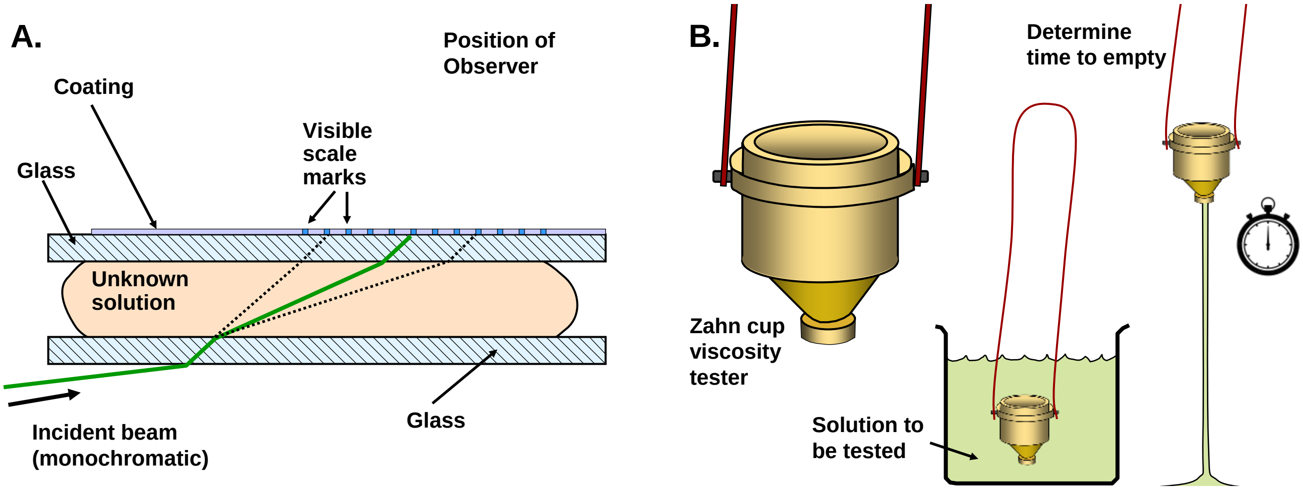


Fig. 13. Common methods for determination of solids and viscosity of prepared starch solutions. A: Refractive index test to determine solids; B: Zahn cup test for viscosity

Gel permeation chromatography

Though viscosity measurements are clearly related to molecular mass of starch in solution, sometimes it is desirable to obtain more precise and detailed information. By means of gel permeation chromatography (GPC), one can reliably obtain molecular mass distributions of polymers used at the size press (Stone and Krasowski 1981; Dong *et al.*

2014; Duan *et al.* 2021). However, none of these cited articles addresses the issue of what to use as a GPC standard when evaluating branched soluble polymers, such as amylopectin.

Analysis of Starch in Paper

Iodine tests

The simplest way to detect the presence of starch, and sometimes to estimate its concentration, involves tests with iodine-iodide standard solutions (Minick *et al.* 1991; Bowles 1995; Svensson and Kloo 2003; Hubbe *et al.* 2019). Swanson (1947) showed that the color of the complex shifted from red to lavender and then to blue with increasing chain length of polysaccharide. It appears that the hydrophobic core of the V-type helix serves as a stabilizer for the iodine oligomers. The way such assays work is by forming a type of linear iodine chain inclusion compound involving the V-type helix form of starch (Immel and Lichtenthaler 2000; Svensson and Kloo 2003). Figure 14 illustrates this mechanism. The precision and scope of such assays is limited, however, by the fact that they such complexes are weak in the case of amylopectin (Swanson 1947) and are not useful for the A-type or B-type helical forms of starch (Immel and Lichtenthaler 2000), including the corresponding retrogradation products. In addition, the iodine complexation tends to be weakened or changed somewhat in hue for substituted starches, such as cationic starch. Thus, when quantification is the goal, a supplementary method may be needed. Vähäsalo and Holmbom (2004) showed that more reliable results could be obtained by using more than one wavelength during iodine-based analysis of starch concentrations in aqueous specimens obtained from paper machines systems. Further interference to iodine-based estimates of starch concentrations can be expected when specimens include either brown fibers, *e.g.* unbleached kraft pulp, or the associated dark process water.

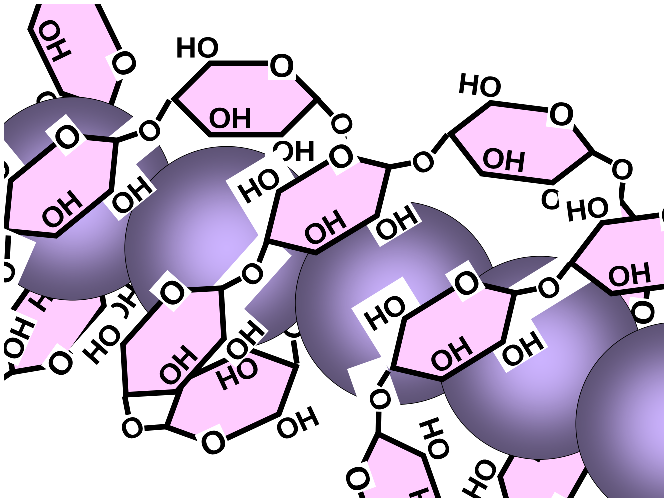


Fig. 14. Schematic illustration of a five-member linear iodine oligomer situated within a V-type helix of amylose. Figure copyrighted by the author and previously published in Hubbe *et al.* (2019).

Sugar analysis after amylase treatment

To gain quantitative information of starch quantities, either in solution or within a paper specimen, a preferred method employs enzymatic hydrolysis, followed by analysis of the component monomeric glucose. The latter can be detected and quantified by the elution time and peak size detected by high-performance liquid chromatography (Birosel-Boettcher 1993).

Tests for amylose vs. amylopectin

Jarvis and Walker (1993) and Sene *et al.* (1997) developed spectrophotometric procedures for determination of the amounts of both amylose and amylopectin in starch specimens. Coloration resulting from iodine complexes was evaluated at different wavelengths, allowing suitable prediction. Based on the differing affinities of amylose and amylopectin for iodine, Herrero-Martínez *et al.* (2004) developed a method based on capillary electrophoresis. As shown by Grant *et al.* (2002), the ratio between the two forms of starch also can be determined based on gel permeation chromatography.

Other natural polymers

No other natural polymer has challenged starch products for dominance in papermaking applications. However, due to some unique characteristics, there are reasons to consider increased usage in the future of both chitosan and guar gum. Carboxymethylcellulose (Oakleaf and Janes 1977; Poranen and Kataja 2000; Gencoglu *et al.* 2010; Kim *et al.* 2017), methylcellulose, and alginates also have been applied at the size press in the past (Cushing 1979).

Chitosan holds the unique status of being the only natural product that, after suitable processing, has a positive charge in solution. Its main source has been crustacean shells, which can be ground and treated with acid and proteinase to obtain chitin; further treatment with NaOH deacetylates the chitin to form chitosan (Younes and Rinaudo 2015; Kim 2018). The deacetylation reaction is shown in Fig. 15.

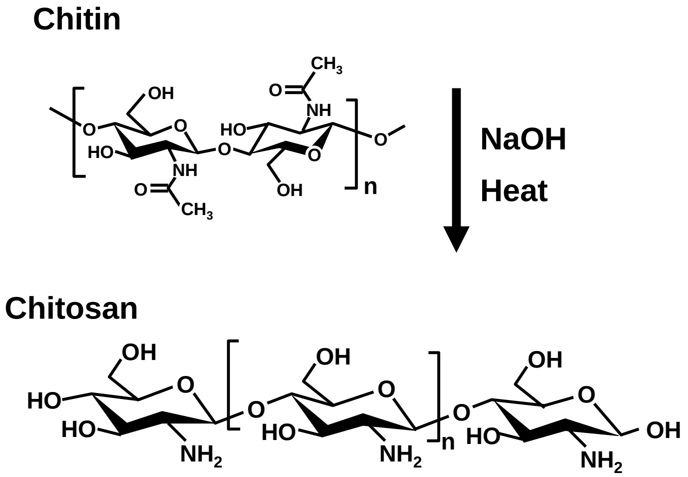


Fig. 15. Key processes in the preparation of chitosan from chitin

Analogously to cationic starch, chitosan's cationic charge could be expected to favor hold-out of its films near to the surface of paper. But a further inherent advantage of chitosan is the fact that its dried films tend to take on a weakly hydrophobic nature. It has been proposed that such hydrophobic character can be attributed to a reorientation of the chitosan chains during the drying process (Hubbe 2019). Challenges that face large-scale implementation of chitosan at the size press include not only its current price, but also its limited conditions of solubility. Solubilization of chitosan can be obtained in a dilute solution of acetic acid (Pillai *et al.* 2009), whereas typical size-press formations have been prepared with higher pH values. Bhardwaj *et al.* (2021) achieved higher levels of water repellency when using different degrees of acetylation of chitosan as a surface treatment for printing and writing paper.

In the case of guar gum, the unique features that make it attractive, perhaps for some specialty paper grades, include its high molecular mass, good solubility, and strong contributions to bonding strength. Challenges to widespread implementation include the much lower amounts produced, compared to starch products, and the fact that most of the guar comes from just one region, consisting of India and Pakistan (Gresta *et al.* 2018).

Synthetic Polymers

Polyvinyl alcohol

Among the water-soluble synthetic polymers, by for the most often mentioned in the published literature is polyvinyl alcohol (PVOH). Positive attributes of PVOH include its ready solubility in water, its availability in different molecular mass ranges, such that different viscosity levels can be reached, along with suitable and the strength and toughness of its dried films. For instance, Bhardwaj and Bhardwaj (2018, 2019) showed increasing tensile strength in both machine- and cross-directions of paper with increasing proportions of PVOH relative to starch at the size press. Figure 16 shows the main synthetic route of PVOH, by way of polyvinyl acetate (Goodship and Jacobs 2005).

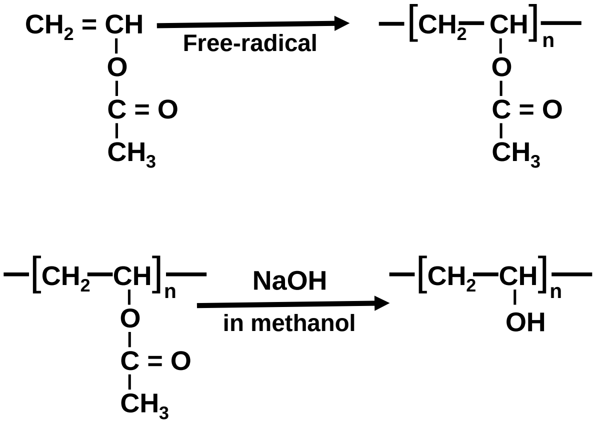


Fig. 16. Preparation and chemical structure of polyvinyl alcohol (PVOH)

Hydrophobic Additives

There are many applications of paper in which resistance to aqueous fluids is critically important, or at least can provide performance advantages. For example, even when making xerographic papers, which are intended mainly for dry application of meltable toner particles onto the paper, some customers may use the paper with an aqueous-based inkjet printer. Paper products prepared using a size press also may be included in packaging, which can get wet during transportation or cold storage. Options that can be considered to provide some of the needed water resistance by size press application include alkylketene dimer and various copolymer products (Latta 1997; Iselau *et al.* 2018; Bildik Dal and Hubbe 2021). Other optional hydrophobic additives for the size press include rosin (Fineman and Hoc 1978b; Kitaoka *et al.* 2001), and black liquor from the kraft pulping of conifer species (Han and Cho 2016). In both of these last cases, the presence of aluminum sulfate (papermaker's alum) in the sheet or added to the size press formulation was required to achieve the desired effects. In addition, hydrophobically modified starch products have been used (McQueary 1991; Jonhed *et al.* 2008; Jonhed and Järnström 2009). The latter authors employed starch that had been derivatized under alkaline conditions with long-chain alkyl chains terminated with quaternary ammonium groups. Kopacic *et al.* (2018) took advantage of the relatively hydrophobic nature of technical lignins to contribute hydrophobicity and other properties by size press addition. Likewise, Wang *et al.* (2014, 2015c) showed that collagen, obtained from leather shavings, provided a substantial contribution to paper's water resistance, when used in combination with either AKD or a styrene-acrylate copolymer. Silane-type compounds also have been shown to be effective as a hydrophobic treatment for the size press (Peng *et al.* 2011).

Alkylketene dimer (AKD)

AKD is a monomeric product that falls into the category of a reactive hydrophobic sizing agent (Ehrhardt and Leckey 2020). When heated, as during the later stages of conventional drying of a sheet of paper, the reactive diketene rings can react with the –OH groups of starch, hemicellulose, and cellulose, thus achieving covalent links of the hydrophobic pendant alkyl groups by means of ester bonds (Dumas 1981; Hubbe 2007; Ehrhardt and Leckey 2020). Though this technology is well known and is often employed at the size press (Stankovska *et al.* 2014; Yang *et al.* 2016; Bildik Dal and Hubbe 2021), there are two well-known issues that need to be kept in mind. First, over-use of AKD may render a paper product too slippery, which can be attributed to the waxy nature of AKD. Second, AKD is notoriously rather slow to react, and the curing process might not be fully achieved during the somewhat abbreviated re-drying of the paper web after a size press.

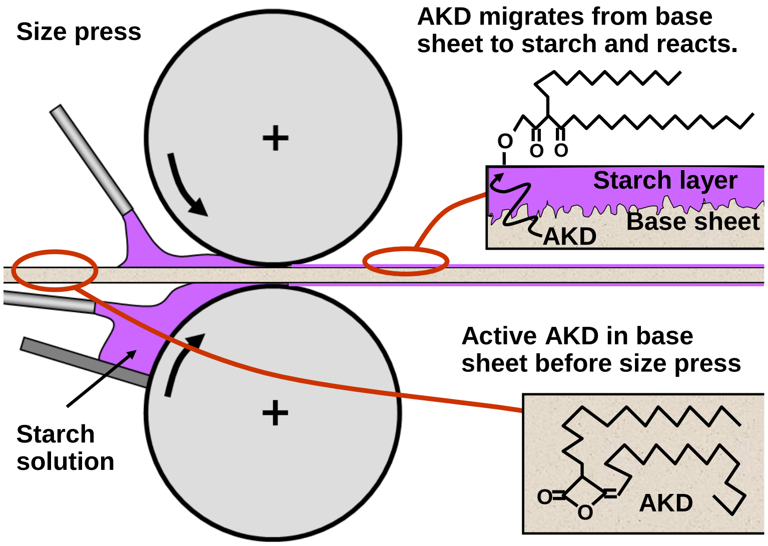


Fig. 17. Sketch of a hypothetical hydrophobizing effect when unreacted AKD sizing agent in the base sheet is able to migrate (probably surface migration) and react with OH groups of freshly deposited starch

Researchers studying the optimization of AKD sizing systems have noticed an interesting synergy between the usage of AKD in the base sheet of paper and the resulting water hold-out properties of the final paper. Sometimes by increasing the moisture content of the paper entering the size press, thus delaying the curing of the AKD that was added at the wet end of the machine, the final hydrophobicity of the paper was higher after the size press starch had dried (Brungardt 1997). The effect was attributed to a reaction between the originally added AKD and the size press starch. As illustrated in Fig. 17, the reported findings are consistent with a process whereby unreacted AKD migrates over distances at the micrometer scale and reacts with the newly-deposited starch, thus contributing to hydrophobicity of the resulting paper.

Hydrophobic copolymers

The topic of hydrophobic copolymers used at the size press already has been reviewed recently (Bildik Dal and Hubbe 2021). Important points will be covered here. It has become a well-established practice to add various synthetic copolymers to the size press starch formulation (Gray and Rende 2005). In particular, such copolymers are formulated to have balance between hydrophilic and hydrophobic groups. Usually, the main purpose has been to meet hydrophobic sizing specifications, *e.g.* the Hercules size test (TAPPI Method T530), or the Cobb test (TAPPI Method T 441) during the manufacture of printing paper products. The mechanism of action appears to involve the diffusion of the hydrophobic copolymers towards the air interfaces during the drying process, as well as the molecular orientation such that many of the nonpolar groups, such as styrene, end up facing outwards from the paper surface after it has been dried (Bildik Dal and Hubbe 2021). A similar tendency of migration to the paper surface during the drying process has been reported in the case of starch products that have been hydrophobically modified (Anttila *et al.* 2012). As described below, some of the best-known copolymer additives for the size press formulation are styrene-maleic anhydride (SMA), styrene acrylate (SA), and alkyl urethane copolymers. In general, the performance of such copolymers in conferring hydrophobic character to paper is favored by the efficient hold-out of the size press formulation near to the paper surface (Batten 1992). Ferreira *et al.* (2009) showed the Fourier transform infrared spectrometry can be used as a sensitive way to probe the distribution of styrene copolymers within a cross-section of paper.

Styrene maleic anhydride (SMA)

The basic molecular structure of an SMA copolymer is shown in Fig. 18 (Barker *et al* 1992; Fischer 1999; Costa *et al.* 2010).

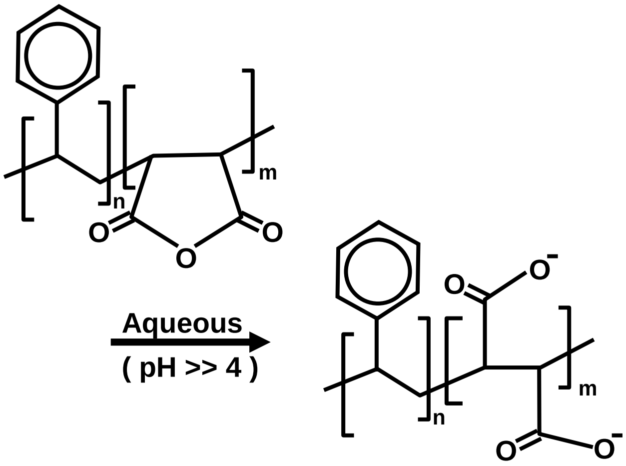


Fig. 18. Chemical structure of styrenemaleic anhydride (SMA) copolymer, also showing its hydrolyzed and dissociated form after placement in neutral to alkaline pH aqueous media (with complete conversion to the carboxylate form if the pH is much greater than 4)

The monomers are expected to have a quasi-random grouping. Placement of the anhydride form of SMA into an aqueous solution at a pH of 6 or higher can be expected to open up the anhydride rings and bring about deprotonation of the resulting carboxylic acid groups. This ionization will contribute to solubility of the copolymer in water. In principle, by varying the ratio between the styrene and the maleic anhydride functions, one can achieve a suitable balance of properties. There needs to be enough hydrophilic character to allow the copolymer to disperse well in the aqueous media (presumably as a form of micelles) but enough hydrophobic character so that the final dried films are able to resist water. To prepare a more hydrophobic copolymer version, some of the carboxylic acid functions can be esterified with alkyl chains (Shibihara and Tominaga 1975; Batten 1995; Bildik Dal and Hubbe 2021).

Styrene acrylate (SA)

Copolymers of styrene and various acrylic monomers have provided alternatives to SMA products (Batten 1992; Barker *et al.* 1994; Chen *et al.* 2015; Chen *et al.* 2017). A main selling point, at least in early years, was a lower forming tendency in comparison to SMA products (Barker *et al.* 1994; Fischer 1999; Thiele and Hauschel 2001).

Urethanes

A high degree of hydrophobicity can be achieved by addition of certain alkylated urethane copolymers to the size press formulation (Pask 1982; Batten 1992). Because the hydrophobic character is provided by linear alkyl chains, rather than styrene, the resulting paper surfaces can be expected to have reduced adhesion to xerographic toners (Thiele and Hauschel 2001).

Latexes

By an optimized level of crosslinking, during their preparation, various copolymers of styrene and acrylic monomers, among other monomers, can be prepared as latex suspensions. In other words, the material is supplied to the paper mill as a colloidally stable dispersion rather than as a solution. Such products can be used to provide hydrophobicity to paper after their addition with starch at a size press (Sousa *et al.* 2010; Xu and Hu 2012; Stankovska *et al.* 2014; Wang and Fang 2015; Abhari *et al.* 2018a,b). This approach has been found to be less susceptible to undesired development of foam (Özdemir *et al.* 2017; Wang *et al.* 2018). Sajbel (2005) stated that acrylic emulsion type size press additives tend to contribute to better adhesion of xerographic toner to the paper; the styrene groups are expected to have good mutual solubility with the binders used in many toners (Chen *et al.* 2015).

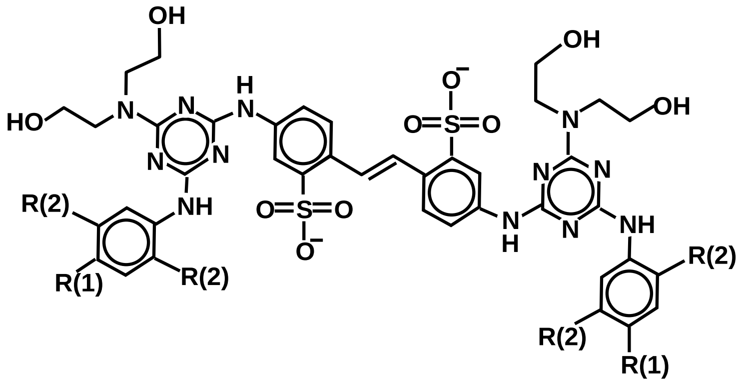
Fluorescent Whiteners and Colorants at the Size Press

Due to similarities in both chemistry and behavior, there is reason to regard fluorescent whiteners, as used by papermakers, as falling into a similar category as the kinds of dyes that are used to control the color attributes or white paper grades or to make various different colors of paper. The most commonly used compounds of both types have an anionic charge, which is provided by sulfonate groups. Extended conjugation, involving alternating double and single carbon-to-carbon bonds – with incorporation of aromatic groups – give rise to the chromatic effects (Hubbe *et al.* 2019).

Fluorescent whitening at the size press

In the case of fluorescent whitening agents, addition of the agent at the size press makes logical and practical sense for two reasons. First, as already mentioned, essentially 100% of what is added substance gets incorporated into the paper, whereas at the wet end, some may potentially be lost to the wastewater treatment system, depending on the retention aid system and other factors. Second, by positioning the FWA compound near to the surface of the paper, there is a greater chance that the incoming UV light will strike it first. Otherwise, it might be absorbed by such materials as TiO_2 or other UV-absorbing compounds that may be present. On the negative side, if FWA is added only at the size press, then UV illumination may reveal an orange-peel-like effect, which arises due to film splitting as the sheet exits the size press nip (Reglat and Tanguy 1998; Triantafillopoulos and Smith 1998; Roper *et al.* 2022). Papermakers often run trials to determine which point of addition, including the option of dual application, makes the best sense, depending on the equipment and the paper grades being made.

Near the beginning of this article, a case study was described in which the relative solubility of the FWA was varied by selecting products having different amounts of negatively charged sulfonate groups. Examples are illustrated in Fig. 19 (Sample *et al.* 2021). By selecting a hexasulfonated FWA product, the papermaker maximizes its solubility, such that it can better diffuse within the paper sheet during and immediately after its application. Sometimes papermakers prefer the tetrasulfonated product, even for size press usage, due to its greater retention onto fibers if and when it gets incorporated into the broke handling system of a paper machine.



Fluorescent whitening agent types:

Di-sulfonated FWA: R(1) = R(2) = H
Tetra-sulfonated FWA: R(1) = sulfonate; R(2) = H
Hexa-sulfonated FWA: R(1) = H; R(2) = sulfonate

Fig. 19. Chemical structures of di-, tetra-, and hexa-sulfonated version of FWA, of which the hexa-sulfonated version is most suitable for size press usage due to is high water-solubility and ability to diffuse locally within the paper sheet before it dries

Dyes and their selection for the size press

Dyes can be used either exclusively at the size press or as a means to correct any two-sidedness problems that remain following wet-end dyeing (Lips 1981; Hubbe *et al.* 2008a). Since the most commonly used papermaking dyes will be compatible with aqueous solutions of starch products, some of the highest priority issues will involve accurate color-matching. Because papermakers will have no control over the kinds of lighting employed by customers to check the accuracy of colors of paper products to physical standards, there is an inherent danger of metamerism. In other words, even if the product and the standard appear to be exactly the same under one set of lighting conditions, they may differ when viewed under different kinds of lighting, including incandescent lamps, simulated northern daylight, fluorescent lights of different types, or LEDs. Such problems can be minimized by choosing a set of blue, red, and yellow dyestuffs that each match the hues of the dyes that were used to make the standard (Hubbe *et al.* 2008a).

As in the case of the FWAs, as just discussed, dyes used at the size press should be selected from those having relatively low affinity for starch or fibers. Thus, a cationic direct dye, which attaches strongly and almost irreversibly to negatively charged substances, should be an especially bad choice when using potato starch or a hypochlorite-oxidized starch at the size press. The tight binding would tend to prevent the dye from diffusing within the paper. Instead, the immobilized colorant would tend to emphasize any orange-peel effect due to the splitting of the starch film after the size press.

Size press correction of "sidedness" of coloration

In paper mills that specialize in colored paper products, it can be a challenge to accurately achieve the desired color specification simultaneously on both sides of the sheet. This circumstance often can be attributed to the usage of traditional Fourdrinier forming technology, in which water is drained from the web in one direction. Such practices can lead to non-uniform composition and structure as a function of position in the thickness dimension of the paper. For instance, dyes that are favorably attached to mineral particles may tend to be washed away from the wire-side of the paper due to the action of hydrofoils (Zeilinger and Klein 1995). Or, more commonly, the higher light scattering ability of filler particles may require that more color needs to be added to the side of the paper that is more enriched in filler content. Fortunately, modern size press technologies allow separate preparation of size press formulations for the two sides of a paper sheet. Figure 20 illustrates a hypothetical system with "size press correction" of color two-sidedness of dyed paper.

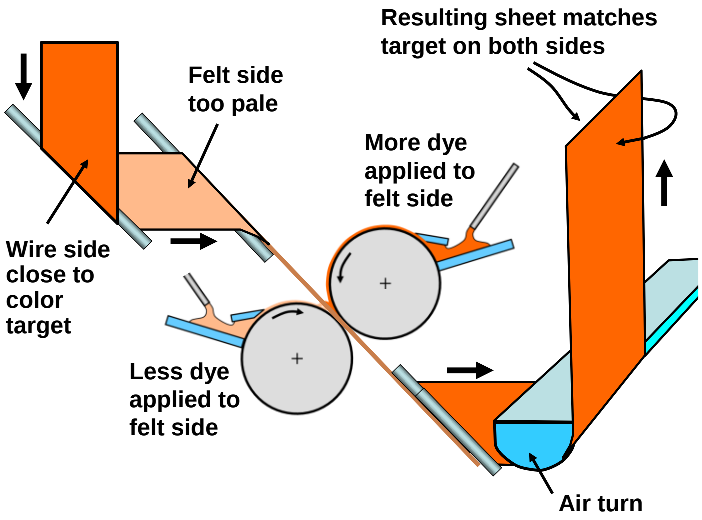


Fig. 20. Illustration of size press correction for color differences between two sized of a paper sheet that has been colorized at the wet end of a Fourdrinier paper machine

Over the course of several turn-ups of the paper reel, the operators can adjust the amounts of dyes to each side of the sheet until color-matching has reached specifications on both sides of the sheet. Technology related to the “air turn” device depicted in the figure has been described by Rennes (1998a,b).

Other Additives

Certain additives, which may be very minor in proportion, can take on important roles in size-press operations. These include crosslinkers and defoamers.

Crosslinkers

One of the main purposes of a crosslinking agent can be to prevent resolubilization of some kind of an aqueous coating if it happens to get wet again later. Crosslinkers for use in size press formulations have been mentioned by several researchers (Trouve and Takala 1993; Li *et al.* 2022; Fei *et al.* 2011; Li *et al.* 2012; Wang *et al.* 2015a; Wang *et al.* 2018; Liu *et al.* 2021; Aguado *et al.* 2022; Li *et al.* 2022). There is a lot of variation within the reagents and approaches in the group of citations. These include glyoxal, silane compounds, and epoxy chemistries, among others. In some cases, crosslinking was used in the usual way, to insolubilize the material after its application to paper. In addition, crosslinking can be used as a way to build up the molecular weight of some sort of copolymer in preparation for its later usage at a size press (Li *et al.* 2012; Li *et al.* 2022). In another case, the researchers used crosslinking to make sure that cyclodextrin, the purpose of which was to collect oil, was not subject to later detachment from the paper (Aguado *et al.* 2022).

Defoamers

Because water-soluble polymers often serve as stabilizers for foam bubbles and because size press formulations come into contact with air during their transport to the size press and back to the run tank, there is reason to anticipate the development of foam (Vines *et al.* 1998; Walter 1998; Fischer 1999). In other parts of the papermaking process, one would counter such tendencies by the usage of suitable defoamer products, which all involve some form of a surface-active agent having a low solubility in water (Avery-Edwards *et al.* 1994; Dencov 2004). Defoamers are also used in the size press system (Wilson 2005). The size press has potential to provide greater challenges than most other papermaking applications due to the much higher concentrations of the polymers. In addition, the surface-active nature of defoaming agents can work against the intended effects of hydrophobic agents, such as styrene acrylamides of SMA products, when they are being used. For these reasons, it may be necessary to try different defoamer products and dosages to find the best compromise.

RUNNABILITY AT THE SIZE PRESS

When using the equipment described in the first main section of this article, together with the material, solutions, and dispersions described in the second main section, one of the key issues to consider is the operating efficiencies that can be achieved. Success in applying a relatively uniform layer at the paper surface involves rheological phenomena, and these are affected by many factors. Some of those factors involve changes over time of the starch material as a result of different process steps. Some factors affecting process efficiency are related to the equipment, the chemistries, and interactions between different components. In particular, the paper web can break as a result of holes in the paper, other defects, or due to a general weakening of the sheet due to excessive rewetting. In the following subsection, effects on runnability on running conditions, such as temperature, solids, amounts applied, nip pressure, and web speed will be considered.

Running Conditions

Some key priorities associated with running a size press operation involve the smooth passage of the formulation into the press nip, an optimized degree of penetration into the paper surface, and suitable properties of the resulting paper products. These goals have been reported to be affected by a variety of factors, as discussed below.

Though there are many constraints imposed by the equipment and materials being used at a paper mill, the operators often have control over many independent variables. These include, but are not limited to the following:

- Temperature of the size press formulation
- Solids of the soluble polymer in the formulation
- The degree of polymerization (as a way to control viscosity)
- Nip pressure at the size press
- Mineral content and type of mineral, if relevant
- Amount applied, especially in a film press system

Dobbs (1993) had proposed that the size press can be envisioned as having four zones, which are illustrated in Fig. 21.

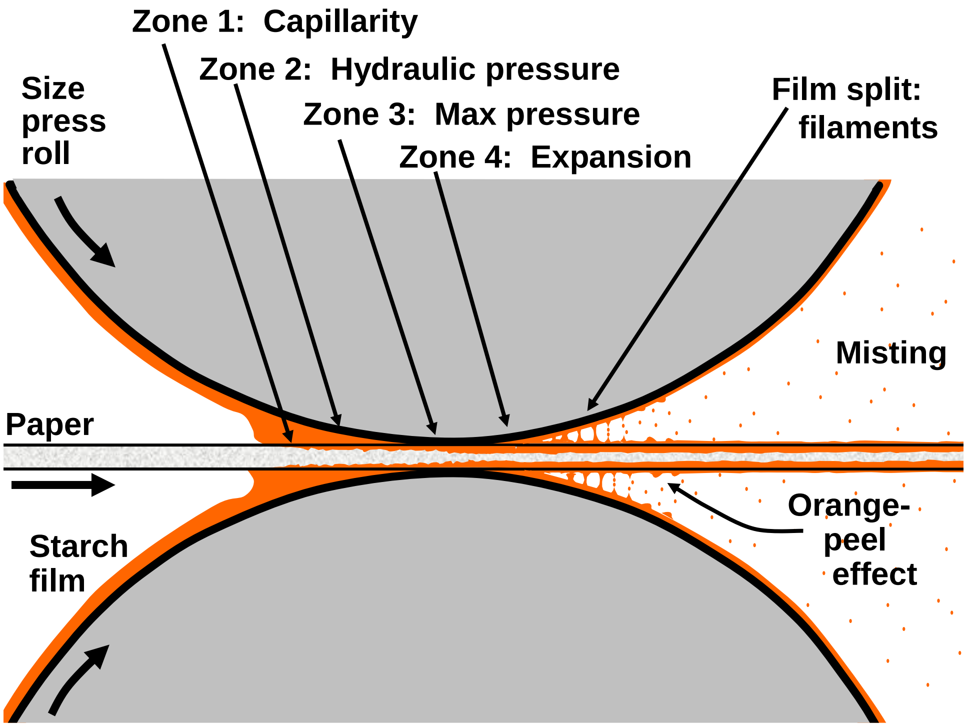


Fig. 21. Hypothetical zones of a generic size press operation

In the first zone, called the absorption zone (which would be expected to play a larger role in flooded nip size presses), it would be expected that capillary action would play a major roll, along with a major influence of hydrophobic character of the base sheet in resisting absorption. In the second (hydraulic pressure) zone, penetration of formulation into the base sheet is expected to depend strongly on sheet porosity (see later). In the so-called maximum pressure zone, the forces driving penetration may be higher, but compression of the web and resulting decrease in porosity may retard the penetration of formulation into the sheet. Then, in the expanding zone, the elastic recovery of the web can be expected to draw some more of the size press formulation into the pore spaces of the sheet.

Temperature

The temperature of a size press formulation will be expected to affect the solution's viscosity, as well as the solubility of various components. For instance, the viscosity of water is known to decrease to 0.47 times its initial value as the temperature is raised from 20 to 60 °C (Korson *et al.* 1969). Analogous changes, though in a somewhat higher range, can be expected with dissolved starch of a fixed amount and degree of precipitation are present. In principle, a lower viscosity of a fluid is expected to provide a proportional increase in the speed of permeation into a porous solid (Darcy 1856). In the case of solutions of polymer in liquid media, viscosity often increases moderately with increasing temperature (Fox 1962). This is consistent with an expected increasing radius of gyration as the solvent conditions improve (Miyaki and Fujita 1981).

According to Cushing (1979), the temperature of a starch formulation is often controlled within the range of 51 to 55 °C in the run tank feeding the size press. Sajbel (2005) gave about 65 °C as likely temperature at most size presses. A relatively hot temperature is consistent with the fact that it is typical to use the starch solution immediately after the cooking process. Assuming that the cooking process has been carried out at about 90 °C or higher, reasons to lower the temperature before application may include safety and avoidance of excessive premature evaporation, which could lead to formation of skins and crusts at the waterlines of wetted equipment.

Howarth (1968) observed a moderate increase in the pick-up of size press starch solution with increasing temperature. The cited work was carried out with a flooded nip size press. It is notable that such application systems would allow more time for possible swelling of the base-stock, which would tend to increase the sizes of pores, through which size press solution could pass.

Mesic *et al.* (2004) made drawdowns of two kinds of starch solution at room temperature and at 70 °C. The resulting paper properties were compared for oxidized starch and a hydrophobically modified starch, having dodecyl linear alkyl groups. The higher temperature application led to much higher levels of hydrophobicity, when using the alkylated starch. The application temperature did not appear to affect any of the measured results in the case of the applied oxidized starch solutions.

Solids

With the increasing usage of film press technology, studies have been carried out exploring the effects of increasing starch solids. Klass (1998) notes that such technology often had been applied with solutions of about 5 to 18% starch. These values were contrasted with a range of between 30 and 65% solids for a traditional aqueous coating formulation, which is usually dominated by mineral particles and either starch or latex binder. On the other hand, flooded nip operations often have lower solids content, *e.g.* 10% or below. As noted by Lipponen *et al.* (2004), a higher solids content is expected to decrease the amount of energy needed for evaporative drying of the paper, in addition to decreasing the frequency of web breaks at the size press.

As will be discussed later in more detail, the maximum practical levels of starch solids have been found to be related to the development of misting at the size press and orange-peel features left on the paper surfaces after the size press (Grön *et al.* 1996; Letzeilter and Eklund 1997).

Viscosity

The viscosity of a starch solution can be viewed as the consequence not only of temperature and solids content, but also molecular mass and some details of the starch composition. Some studies that particularly dealt with the effects of viscosity on size press outcomes are listed in Table 4.

Table 4. Studies Considering Effects of Formulation Viscosity on Size Press Outcomes

Topics of the Research	**Citation**
At low production speeds, with a flooded nip, pick-up decreases with increasing viscosity, but the reverse becomes true at high paper machine speed.	Hoyland *et al.* 1977
Starch penetration is enhanced by low viscosity of the formulation.	Remmer & Eklund 1992
It is important to measure viscosity to monitor the degree of conversion of size press starch.	Dobbs 1993
Viscosity of a formulation can be measured using nip pressure and torque. Pigmented coating formulations show dilatancy at the highest shear rates.	Alonso *et al.* 2000
Carboxymethylcellulose (CMC) was found to increase the high-shear viscosity of a calcium carbonate suspension	Poranen & Kataja 2000
Increasing starch solution viscosity decreases pick-up, but only when contact with the starch solution is brief before the nip.	Shirazi *et al.* 2004

Nip pressure

Especially at high production speeds, the pressure applied at a size press nip has been shown to have a relatively large influence on how deep into the paper the starch penetrates in a film press operation. According to Gray and Rende (2005) the nip pressure in a modern size press is often in the range of 25 to 30 kN per linear meter of nip. Research that has considered such relationships are highlighted in Table 5.

Hoyland and Howarth (1972) derived practical predictive equations for size press pickup based on the viscosity of the formulation and the speed. The three terms in their equation were related to the sheet (a constant uptake), an absorption term (inversely related to both speed and viscosity), and a hydrodynamic term (proportional to both speed and viscosity). The sheet term was found to depend on the extent of refining of the fibers, which is related to the resulting permeability of the paper. The hydrodynamic term was further shown to be a function of roll radius, nip loading pressure per linear width of the nip, and a roll deformation factor.

Table 5. Nip Pressure and Related Factors Affecting Penetration of Size Press Formulations

Topics of the Research	Citation
Increasing pickup was observed with increasing pond depth in flooded nip applications.	Howarth 1968
Increasing nip pressure decreased pick-up in a flooded nip size press operation; such effects were diminished when using softer roll covers in the size press nip.	Hoyland *et al.* 1977
Increasing uptake with increasing nip pressure was shown over wide ranges of pressure and contact time.	Remmer & Eklund 1991, 1992
Nip pressure had a dominant influence on the degree of size press penetration into the sheet.	Poranen & Kataja 2000
Pressure-induced permeation governs size press pickup.	Forsström *et al.* 2003
Increasing applied nip pressure had a small effect in decreasing starch wet pickup in a one-sided flooded nip laboratory size press.	Shirazi *et al.* 2004
The pressure pulse in a film press nip is much higher than in the case of blade coating, giving rise to greater penetration into the sheet.	Engström 2005

Effects of mineral content on size press runnability

In principle, size press efficiency can be expected to improve if means are found to limit penetration and wetting deep into the core of the sheet. One way to achieve such an outcome would be to add something to the formulation that tends to block pores within the base-sheet’s structure. Since such additives might be expected to also affect viscosity values of the formulations, some aspects related to the previous topic may be relevant. Thompson and Hutto (1997) showed that smectites (*e.g.* sodium montmorillonite or bentonite products) at the 5% level in size press formulation were quite effective in decreasing size press pickup. In addition, the paper after the size press was less porous.

Amount applied

By varying the pressure applied to a metering blade, or various other adjustments, papermakers can control the amount of starch applied at a film press, even when there are differences in solids levels, starch attributes, and viscosity levels. Thus, some studies have focused on the consequences of different amounts of applied starch in size press operations. Such studies are highlighted in Table 6.

Table 6. Research Concerning Effects Related to Starch Amount Applied at Size Presses

Topics of the Research	Citation
The onset of misting problems was found to be a function of the applied amount and other variables.	Grön *et al.* 1996
It is important to decouple the elastic and viscous components of rheology to minimize misting problems, which tend to increase with increasing amount applied.	Gane *et al.* 1997
Applied amounts of starch were in the range 0.7 to 4.0 g/m^2 on each side and pigmented formulations at 3 to 15 g/m^2 per side.	Klass 1998
It is stated that the metering size press can apply 8 g/m^2 per side before film splitting issues become serious.	Wikström & Grön 2003
Metering systems (film presses) can apply 10 to 12 g/m^2 per side.	Gray & Rende 2005

As shown, certain runnability problems are likely to become serious at higher amounts of applied starch. A general finding is that excessive fluid in the nip will give rise to misting. By contrast, if most of the fluid penetrates into the paper, then only a thin film will be involved with the splitting, and related problems will be minimized.

Web speed

The speed of the web ultimately may face a limit when applying a size press formulation. The limit had been found to depend on other factors already mentioned, such as the amount applied. Studies that have dealt with such speed limitations are highlighted in Table 7.

Table 7. Studies Evaluating Practical Limitations in the Speed of Size Press Operations

Topics of the Research	Citation
Pickup first fell and then gradually increased with increasing web speed in flooded nip press (horizontal and vertical).	Howarth 1968
Speeds up to 2000 m/min were achieved with modification of formulations.	Hiorns *et al.* 1996
There was decreasing film transfer to paper with increasing web speed in film press operation, with problems tending to develop with increasing applied amount and speed.	Trefz & Seiz 1998
Sequential application of smaller amounts, using two size press applications allowed pilot application up to 1700 m/min.	Glittenberg & Becker 2000
Runnability problems were encountered at speeds above 1500 m/min.	Voss *et al.* 2002

Colloidal destabilization

Most size press formulations, especially if they contain mineral particles, are prepared in such a way as to achieve a high degree of uniformity, *i.e.*, a colloidally stable formulation. The idea is that the mixture needs to flow smoothly as it passes through a film applicator, as well as thorough a size press nip. However, there are some exceptions that deserve mention here, since they have the potential to affect runnability.

Salt addition has been shown to be effective, in some cases, in changing the viscosity of a size press formulation (Anderson and Järnström 2006). Such treatment was found to decrease the penetration of amphoteric starch. This was said to be consistent with salt-enhanced flocculation of the starch solution, which was used together with a cationic copolymer hydrophobic agent. Such effects are expected to be prominent in the case of the hardness ions Ca^{2+} and Mg^{2+}. As illustrated in Fig. 22, a likely explanation for such behavior is a transient association among adjacent starch macromolecules. One possible outcome of such association could be an increase in viscosity, tending to slow the rate of penetration into pores. Another possibility would be precipitation of material from the solution phase; the resulting particles might be too large to pass into the pores of paper.

The concepts depicted in Fig. 22 were backed up by an observed increase in viscosity in those cases. The opposite was observed in the case of an anionic starch. Similar findings were reported by Seo *et al.* (2020), who used a cationic copolymer of acrylamide to destabilize a starch solution. The destabilized starch formulation tended to stay out nearer to the surface of the paper, thus contributing greater stiffness and resistance to air through the paper. Iselau *et al.* (2018) likewise observed opposite effects of salt addition, depending on whether cationic particles (beneficial effects) or anionic particles (detrimental effects) had been added to size press starch formulations. All of these findings are consistent with an earlier statement by Cushing (1979), who recommended that conditions such as pH and water hardness be carefully adjusted by trial and error to find out what are the most favorable results at size presses. Due to the fact that so few researchers have considered this topic, it seems likely that there is a lot of room for improvement in size press operations through the control of such variables as ionic strength, pH, and water hardness.

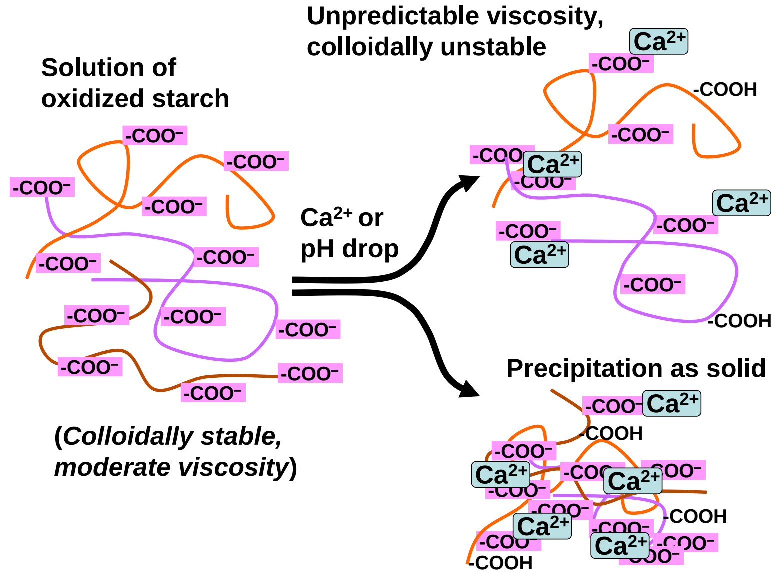


Fig. 22. Likely mechanisms by which partial colloidal destabilization of a starch solution could decrease its permeation into a base sheet

Film Split Problems

In a substantial proportion of the cases described in the articles cited in the preceding subsections, it appears that problems encountered with increasing web speed, application amount, and other factors can be attributed to film-splitting problems at the exit to the size press nip (Trefz and Seiz 1998). Commonly reported problems that have been attributed to film splitting include misting and orange-peel effects.

Mechanistic aspects of problem related to film splitting

As was illustrated earlier in Fig. 21, when certain limitations related to web speed and application amount are exceeded, the splitting of the solution of starch between the paper surface and the adjacent roll becomes irregular. Elongated filaments develop, and these subsequently break up into air-borne droplets (Ascanio *et al.* 2006).

Film splitting phenomena can be influenced by various factors. Ascanio *et al.* (2006) showed that increases in the extensional viscosity of a formulation – often achievable by increasing the concentrations of soluble polymers – can reduce the formation of mist droplets. Oakleaf and Janes (1977) had made a similar recommendation to overcome the problem. However, there have been conflicting recommendations on this point. Salminen *et al.* (1996) recommended reducing the shear viscosity by increased reliance on latex binder and less reliance on carboxymethylcellulose (CMC), which is usually called a water retention agent. Gane *et al.* (1997) recommended preparation of pigmented size press formulations such as to favor rapid immobilization, which usually entails a relatively high pigment solids level, as well as minimization of water retention agents. Likewise, Grön *et al.* (1996), Salminen *et al.* (1996), and Roper *et al.* (1997) recommended using high mineral solids levels and reduced water retention as a means to minimize misting. Such strategies face a practical limit, however, since excessive immobilization can lead to deposition of dried crumbs onto the equipment, such as at a blade used to apply a formulation to the size press roll. Reimers *et al.* (1998) carried out extensive work related to film splitting problems and suggested that the interactions between different factors are sufficiently complex that no general rule can be stated for prediction of such problems. Triantafillopoulos and Smith (1998) suggested that the answer may depend on the details; thus, to minimize problems, water retention is needed at low speeds, but rapid immobilization becomes more important with increasing speed.

Misting

Misting can be defined as the generation of airborne droplets at the exit of a size press nip. Misting is undesirable because the droplets can land on both the equipment and the paper surface. Droplets landing on the equipment might merely create an untidy appearance. Droplets landing onto the sheet may cause the surface to be dusty, especially if the water content in the droplets has become partly or mostly evaporated while passing through the air. Roper *et al.* (1997) observed a bimodal distribution of droplets, and some of the droplets became large at high speeds. As illustrated in Fig. 23, the nature of the mist droplets has been observed to depend on the amount of size press solution applied and the running speed. As depicted in Part A of Fig. 23, at lower weights and speeds, capillary phenomena will tend to dominate. Capillary instability of the filaments will cause them to break up into small droplets, which become fine mist. At higher applied amounts speeds and speeds, as depicted in Part B, the situation will become dominated by centrifugal effects, by which relatively large droplets become flung from the press nip area.

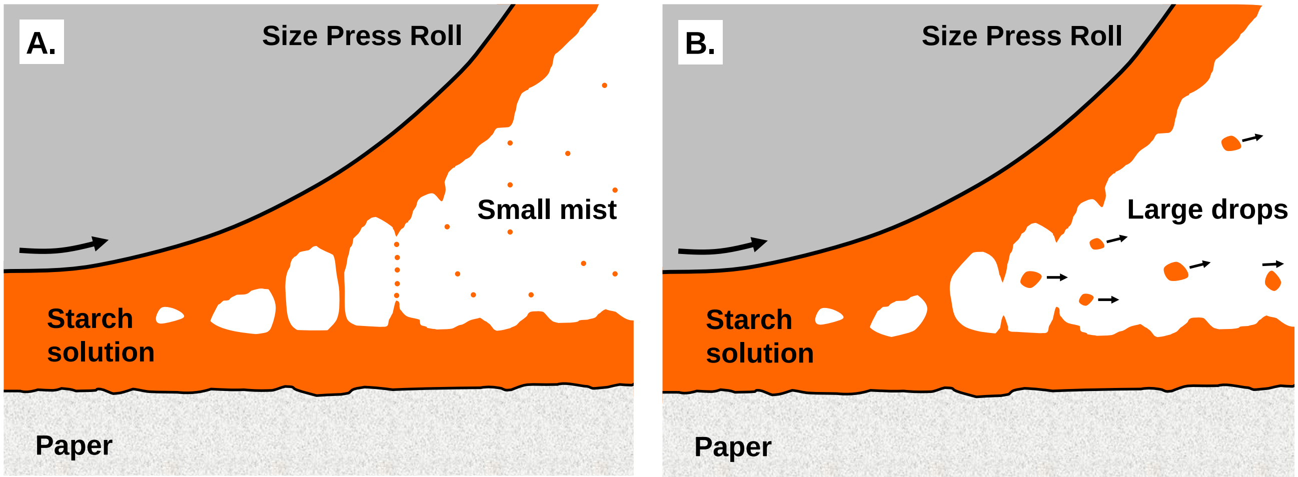


Fig. 23. Contrast between (A) conditions favoring small mist droplets that move by convection of air, *vs.* (B) conditions favoring large droplets for which centrifugal force and momentum are important at the exit of a size press nip

The underlying cause of mist development at the exit of a size press nip, especially at limits of high web speed in combination with high applied amounts, is the breakage and recoiling of filaments of solution that form as the distance between the rolls increases (Ascanio *et al.* 2006). Roper *et al.* (1997) found a correlation between the filament size and the droplet size. Cavitation, which can involve the formation of bubbles due to the high negative pressure generated in the exit region of a size press nip, also has been said to contribute to misting (MacPhee 1997a,b; Ascanio *et al.* 2006). A different explanation for air in the film was made by Alonso *et al.* (2000). They suggested that flow instabilities in the film applicator could be the cause of air entrainment, rather than cavitation. Another likely contribution to film splitting, which is specific to film press operations, is hydrodynamic instability when the starch film begins to enter into the nip between the two size press rolls (El-Sadi and Esmail 2008). The cited authors numerically simulated the flow patterns to predict the presence of vortex flow. Key factors were said to be the inertia and viscoelasticity. Owens *et al.* (2011) used high-speed photography to capture the formation of filaments and their subsequent breakup into droplets; the results were interpreted based on relaxation times.

A third explanation for misting is a tendency for the sheet to follow one of the press rolls after the nip, which may become more pronounced with increasing web speed (Hiorns *et al.* 1996). The situation is depicted in Fig. 24. As shown in this example, the sheet tends to follow the press roll on the right side. Thus, the side of the paper that follows that press roll would be in contact with the roll surface for a much longer period, and the angle at which the sheet leaves the roll is much greater on that side. In principle a higher angle between the departing paper and the roll surface would be expected to decrease the time available for filaments of starch solution to break cleanly and retract, rather than being subject to uncontrolled breakup into droplets.

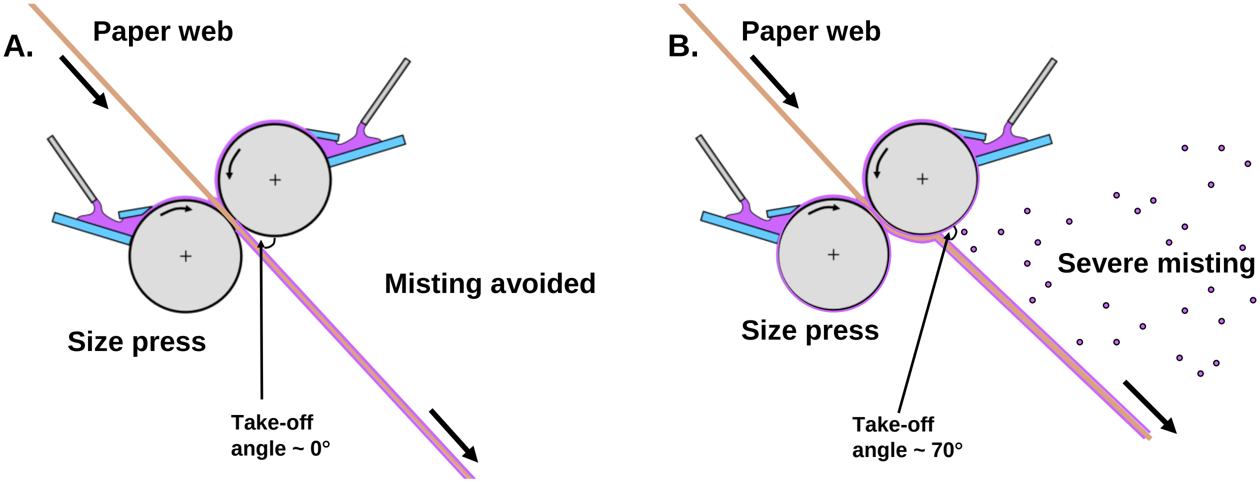


Fig. 24. Illustration of how the take-off angle of paper may be related to the development of misting at a size press. A: straight passage through nip; B: abrupt take-off angle (drawing inspired by Hiorns *et al.* 1996)

Orange peel and ribbing effects

When the stretched filaments of starch formulation break and collapse back onto a paper surface after the exit of a size press nip, the resulting pattern has been called "orange peel" (Hiorns *et al.* 1996; Kogler 1998; Reimers *et al.* 1998; Ascanio *et al.* 2006; Roper *et al.* 1999) or "ribbing" (Reglat and Tanguy 1998; Triantafillopoulos and Smith 1998; Roper *et al.* 2022). Reglat and Tanguy (1998) reported that ribbing was controlled by either inertia or capillary forces. Specifically, inertia was said to govern ribbing phenomena at commercial speeds of about 1000 m/min for thin gaps, whereas capillarity was said to dominate in the case of wide gaps. Because it is possible, sometimes, for the wet starch film to even itself out before it dries, Gray and Rende (2005) said not to expect there to be a strong correlation between filament formation, misting, and orange peel effects. The cited authors reported that orange peel effects can be expected to increase with the use of grooved rods for film application to the size press role, with dispersed air in the formulation, with low solids, and with increasing thickness of the applied layer.

The term ribbing also has been used to describe a wavy thickness profile of a coating, arising due to unstable flow (Carvalho and Scriven 1999; Chong *et al.* 2007). Such waves are shown in a photograph as being parallel and evenly spaced perpendicular to the direction of manufacture (Chong *et al.* 2007). This kind of ribbing can be expected when the operating parameters, computed based on three-dimensional flows, are outside of a defined range (Carvalho and Scriven 1999). The cited authors computed three-dimensional regions of operational space in which such flows can be expected to develop. It was shown that the usage of a deformable roll cover is able to delay the onset of that kind of ribbing. Lie *et al.* (2009) carried out related calculations for rolls having a speed ratio of 1:4.

As a means to decrease the extent of pattern formation, due to the orange peel effect, Oakleaf and Janes (1977) recommended enhancement of the thixotropic nature of the formulation. Such behavior usually is associated with a time-dependent development of structure among particles. Highly platy mineral suspensions, for instance, can develop thixotropy due to a tendency to develop “house-of-cards” structures in low-flow situations (Huang *et al.* 2018). The transient structures break down reversibly, over the course of time, as the mixture is subject to higher rates of shear.

Perhaps in addition to the patterns resulting from film splitting dynamics, the patterns may also be affected by nonuniform structure (*i.e.* poor formation uniformity) of the base sheet (Wikström and Grön 2003). This possibility will be revisited when base sheet effects are considered.

Changes in Starch Solution after its Cooking

A series of partly irreversible changes involving the starch appear to take place during a typical size press starch application. These include retrogradation, further changes associated with drying, and some degree of molecular breakdown is also possible.

Retrogradation of the amylose content

Retrogradation can be defined as a conformation change of the amylose portion of the starch, followed by a form of association between adjacent helices, leading to separation from the solution phase (Fang *et al.* 2020). Figure 25 provides a pictorial representation of the retrogradation process.

Based on the experience of papermakers, the appearance of retrogradation is associated with reduced bonding strength within starch films. To achieve the most favorable results at the size press, there is a preference for using clear starch films in which no precipitate or cloudiness is present. However, the expectation of lower film strength when using retrograded starch is not true in all circumstances. For example, Soni *et al.* 2020) reported higher strength when using retrograded tapioca starch in combination with nanocellulose to make films. The strength of the composite films was higher than when using non-retrograded starch. Factors that promote retrogradation include low pH, low temperature, slow cooling, and the presence of cations such as Ca^{2+} and Al^{3+} (Cushing 1979; Fang *et al.* 2020).

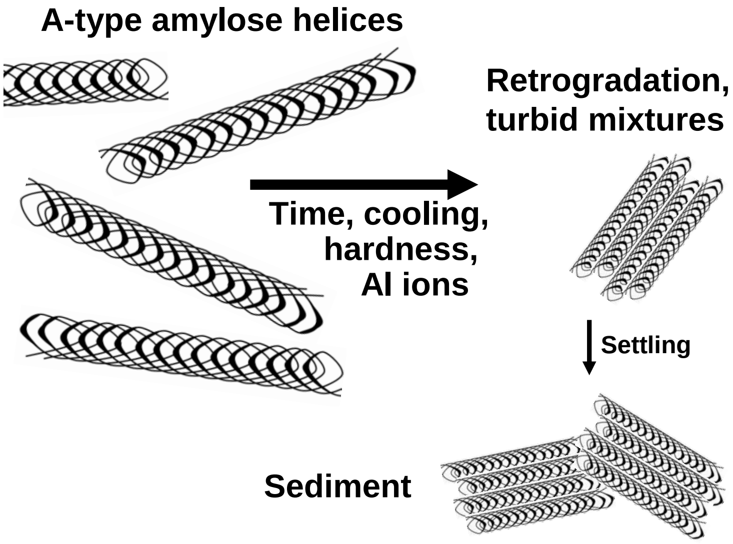


Fig. 25. Illustration of the retrogradation process of amylose in a starch solution, whereby bimolecular helices form, agglomerate, and precipitate from solution

The formation of precipitates in the run tank can settle as sludge, and if such material passes into the size press, it can create imperfections in the paper. For example, it may be necessary to splice the paper web at the winders to remove spots in the paper resulting from starch deposits (Pawlak 2003). The cited work describes how such costly problems can be addressed by filtering the starch solution. By eliminating the development of holes and related blemishes in the paper web, it was possible to avoid the need to continually remove such defects by splicing the paper in the winder operation. In addition, by filtering the starch solution, there was less need to discard starch solution due to excessive sludge levels in it.

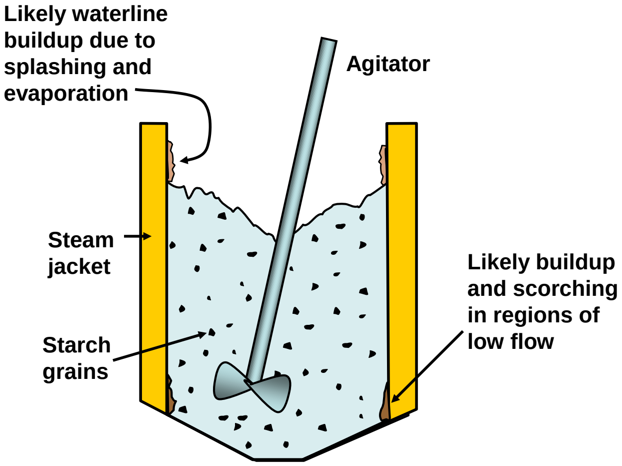


Fig. 26. Water-line evaporation of starch films as a mechanism that may contribute to particulate material present in cooked starch solutions

Effects of evaporation

Because the cooking of starch requires elevated temperatures, it is inevitable that problems related to evaporation of water will be experienced during starch preparation, as the starch solution is metered through piping, within a run tank, and during its application to paper at the size press. For instance, after laboratory preparation of starch solutions it is often necessary to add a calculated amount of water, based on weight, to achieve a target solids level. When using a steam-jacketed vessel to cook starch at ambient pressure, a dried layer of starch can form above the waterline, and this can be a source of particulate contamination if some of the material breaks free. Figure 26 illustrates likely effects of dried starch building up at the waterline of a steam-jacketed tank or in dead zones protected from flow, with the danger that some such solidified material becomes entrained again in the cooked starch solution.

Copolymer deposition

Due to their combination of hydrophilic and hydrophobic groups, the copolymers that are used to contribute to hydrophobicity of paper, by size press addition, tend to be sensitive to aqueous conditions, such as pH, salinity, and the presence of hardness ions. For such applications it is prudent to follow the supplier's guidance regarding suitable "window" of aqueous conditions to maintain in the size press formulation. Figure 27 illustrates the expected effects of either acidification (Part A) or addition of hardness ions (Part B) to a solution of styrene maleic anhydride (SMA) product. Though the general tendency in each case would be to make the copolymer less soluble, testing may be needed to determine what conditions will lead to the onset of either excessive form or precipitated material, *etc.*

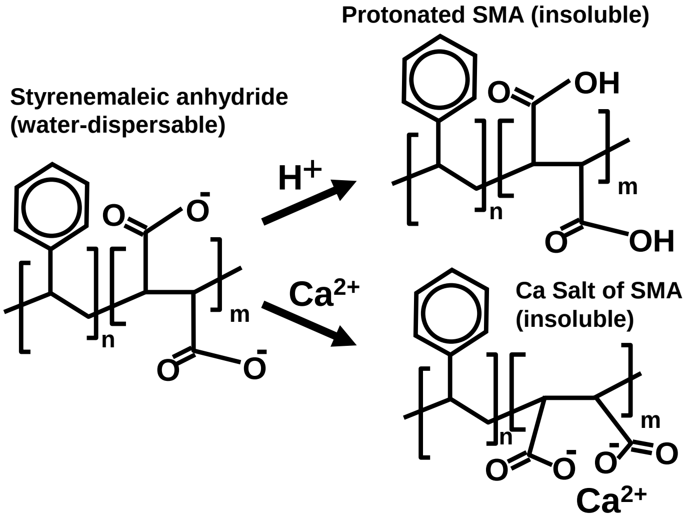


Fig. 27. Water-line evaporation of starch films as a mechanism that may contribute to particulate material present in cooked starch solutions

Biodegradation

Starch is highly biodegradable, mainly through the action of α-amylase, which is widely present in natural environments, *e.g.* human saliva (Butterworth *et al.* 2011). The α-amylase also will be routinely released by bacteria that proliferate within industrial process water, especially when starch is present (Molobela *et al.* 2010; Yang *et al.* 2020). Though the high temperatures associated with size press starch preparation can be expected to denature the enzyme, this will not necessarily stop enzymatic breakdown at other points in the process. While the size press operation is generally free of problems related to bacterial action, there is a high likelihood that starch applied at a size press gets recycled back to the paper forming process; this can be due to the repulping of broke (off-quality or broken paper) or due to paper recycling.

Base Sheet Attributes

Having considered physical issues at the size press, starch formulation issues, including factors related to viscosity, the next topic to consider is the paper base-sheet. Many studies have reported effects of such base-sheet attributes as porosity, moisture content, and hydrophobic sizing on the uptake and "hold-out" of surface-applied starch solutions. Highlights of some studies that focused particularly on base-sheet issues are given in Table 8. Wilson (2005) reported that about 5 s of Hercules Size Test (HST) holdout keeps most of the size press starch near the paper surface; after reaching 15 to 20 s HST, increased wet-end sizing has no more effect. In addition, the topic has been reviewed by Eklund (1989) and Engström (2005).

Table 8. Studies Focusing on Base Sheet Effects on Size Press Operations

Independent Variables Considered in the Research	Citation
Hydrophobic sizing with AKD and filler content with PCC	Cho & Garnier 2000
Precalendering and variation of filler content	Ahlroos and Grön 2001
Porosity and water repellency	Aloi *et al.* 2001
Refining and AKD sizing	Forsström *et al.* 2003
Hercules Size Test (HST) holdout *vs.* size press holdout	Wilson 2005

In Table 8, all of the listed studies were concerned with ways to limit the degree of permeation of size press formulation into the sheet. However, some other researchers have emphasized the need to achieve an optimum degree of permeation (Cushing 1979; Andersson and Järnström 2006; Bhardwaj and Bhardwaj 2019). It seems likely that the emphasis of many researchers on increased hold-out is that the relatively low viscosity and solids levels of typical size press formulations means that excessive penetration is more likely than too little, when the goal is to optimize such attributes as paper stiffness and surface strength (Fineman and Hoc 1978b).

Permeability of the base sheet

The fractional void volume in the base sheet, *i.e.* the porosity, has been shown to be one of the most important variables governing the hold-out of size-press formulation toward the outside layers of a paper web (Hoyland *et al.* 1977; Cho and Garnier 2000; Ahlroos and Grön 2001; Aloi *et al.* 2001; Wikström and Grön 2003; Engström 2005). In simple terms, higher porosity encourages deeper penetration of size press formulation into the base paper. Conversely, denser base paper has been shown to hold out pigmented size press formulations to a greater degree, thus providing more effective coverage of base sheet nonuniformities (Forsström *et al.* 2003).

Based on the viscosity terms used in the Lucas-Washburn analysis of permeation into paper (Lucas 1918; Washburn 1921), it is expected that larger pores will tend to be more favorable for rapid penetration into porous media (Eklund 1989; Shirazi *et al.* 2004; Engström 2005). The following expression shows how the viscous resistance to flow of a Newtonian fluid into a porous material, as represented by uniform cylindrical capillaries, will be related to the best-fit radius of the cylinders (Hubbe *et al.* 2020).

$$\Delta P_{\text{viscous}} = 8\mu v L / r^2 \tag{1}$$

In this equation, $\Delta P_{\text{viscous}}$ is the pressure that is being applied (say at the size press nip) to drive the formulation into the base sheet, μ is the coefficient of viscosity (assuming Newtonian, laminar flow), v is the average velocity in the direction of permeation, L is the wetted length of fluid already present within the capillary, and r is the best-fit estimated radius of the capillary. According to this rule, if the goal is to maximize the hold-out of starch solution at a defined level of porosity, then it would make sense to prepare a base sheet with small pores. One way to achieve such a structure would be to carry out a preliminary pigment coating, but this is seldom done ahead of another size press application. A related approach is to add fillers, such as calcium carbonate particles, to the base stock (Dickson *et al.* 2002; Engström 2005).

Even though the Lucas-Washburn equation has been suggested as a basis for explaining slower permeation of size-press formulations into a based sheet that contains filler particles, such as situation is not well-described by assuming uniform, cylindrical capillaries in the porous material. A more realistic approach has been suggested based on the Kozeny-Carman equation (Engström 2005). Certain forms of that equation are expressed in terms of the surface area per unit mass within the porous structure (Kozeny 1927; Carman 1938; Hubbe *et al.* 2020). The relationship can be shown as follows (Carrier 2002),

$$k = \frac{\varepsilon^3}{k_c S^2 (1-\varepsilon)^2} \tag{2}$$

where k is the Darcy permeability coefficient, ε is the fractional void volume (or porosity) of the packed bed, k_c is essentially a correction factor, which includes *e.g.* the effect of tortuosity, and S is the specific surface area of the solids. Such an approach can be justified due to the relatively small size of typical filler particles, in comparison to the cellulosic fibers, thus increasing the effective surface area per unit mass within the base sheet. Figure 28 contrasts the two simplified models that have been used to account for the resistance to penetrate into porous materials, with the neglect of capillary wettability effects.

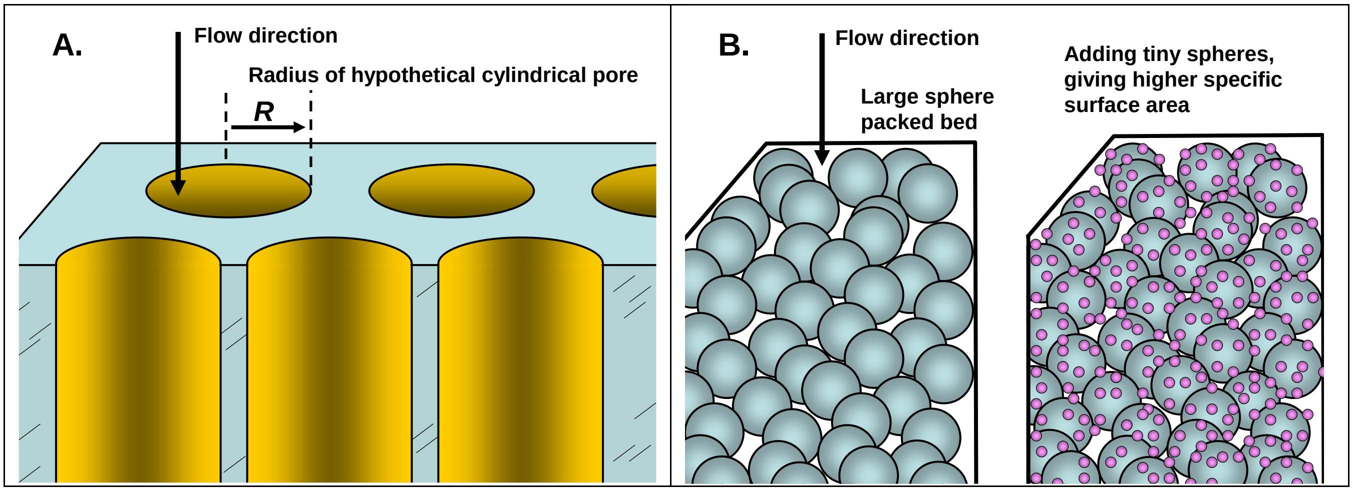


Fig. 28. Contrast between two models of resistance to flow into a porous solid: (A) cylindrical pore model of Lucas and Washburn; (B) surface area-based model of Kozeny and Carman

Hydrophobic sizing of the base sheet

Especially in cases where starch solution is being applied to paper in a flooded nip size press, it has been shown that the amount of penetration into the paper can be decreased by hydrophobic sizing during production of the base sheet. Highlights of such studies are listed in Table 9. To summarize, increasing hydrophobic nature of the base sheet can be expected to reduce the amount of formulation taken up by the paper at the size press (especially in the case of a flooded nip press), thereby decreasing the frequency of web breaks at the size press (Dill 1974; Hoyland *et al.* 1977; Tompkins and Shepler 1991; Cho and Garnier 2000; Carceller and Juppo 2004; Shirazi *et al.* 2004; Li *et al.* 2013). The effect is illustrated in Fig. 29.

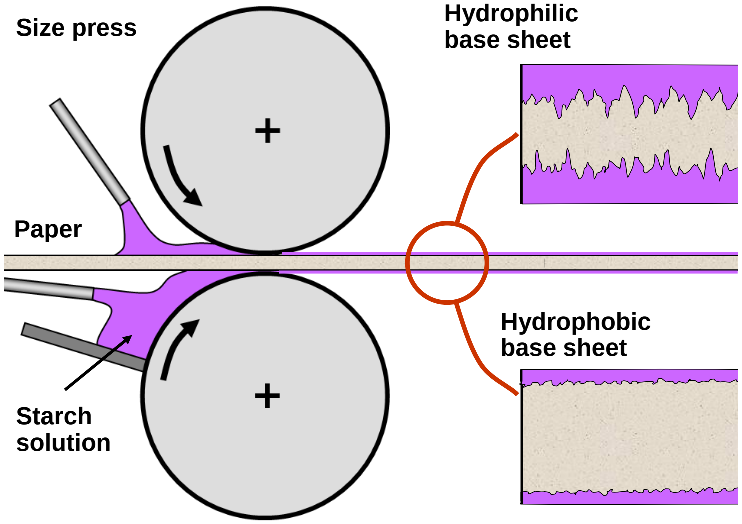


Fig. 29. Suggested mechanism by which hydrophobic nature of a based sheet, due to earlier treatment with hydrophobic sizing agents, results in less penetration of starch into the sheet

Base sheet hydrophobicity has been found to be less important in the case of film press applications, especially when mineral particles were present. In such cases, due to the typically higher solids and viscosity of the starch solution, as well as the very brief time of contact, penetration tends to be dominated by pressure effects rather than capillarity (Eklund 1989). However, other authors report clear effects of internal sizing on the pickup of size press starch even in such systems (Shirazi *et al.* 2004; Wilson 2005; Li *et al.* 2013).

Moisture content entering the size press

A very dry web of paper typically tends to take up less starch formulation at a size press compared to a more moist incoming web. The effect is analogous to people's common experience when using cellulose-based sponges. A sponge that has been sitting dry for a day may at first be rather ineffective at sopping up a wet puddle. But after wetting and squeezing, the same sponge typically is much more effective as an absorbent. The review article by Cushing (1979) reports higher uptake at the size press with increasing moisture of the incoming web. Increased size-press starch uptake by the paper was observed with increasing incoming moisture content in the range of 4 to 8%.

Table 9. Studies Showing Effects of Base Sheet Hydrophobic Character on the Penetration of Size Press Formulation

Key Findings Presented in the Article	**Citation**
In a flooded nip size press, wet-end hydrophobic sizing decreases the uptake amount at the size press.	Dill 1974
Internal hydrophobic sizing of the base sheet results in greatly reduced uptake of starch in a puddle-type size press.	Hoyland *et al.* 1977
Internal hydrophobic sizing of the base paper with rosin and alum helps the size press starch to reduce linting by holding the formulation out toward the surface of the sheet.	Fineman & Hoc 1978a,b
Wet-end sizing of the base sheet is important in order to achieve high efficiency (runnability without breaks) at the size press.	Cushing 1979
When the base paper is rendered hydrophobic, the mechanism of size press uptake switches from capillary-driven to diffusion- and pressure-driven.	Eklund 1989
Internal sizing of the base sheet improved the holdout and performance of size press formulation that included styrene-maleic anhydride (SMA) hydrophobic polymer.	Tompkins *et al.* 1991
Internal sizing of the base sheet increased the effectiveness of styrene-maleic anhydride (SMA) hydrophobic polymer added with size press starch solution.	Brungardt 1997
The absorptivity of the base sheet needs to be minimized in order to improve size press runnability.	Triantafillopoulos & Smith 1998
Wet-end hydrophobization with alkylketene dimer (AKD) decreased the amount of surface size taken up by the paper in a laboratory flooded nip size press.	Cho & Garnier 2000
Interaction of alum in the base sheet decreases permeation of size press formulation that includes a hydrophobic copolymer.	Aloe *et al.* 2001
When using a film press for a pigmented coating, the results do not depend on the hydrophobic nature of the base sheet.	Forsström *et al.* 2003
The base sheet was internally sized with alkylketene dimer (AKD) to enhance surface sizing with starch and a styrene-acrylate ester copolymer.	Carceller & Juppo 2004
Surface size uptake fell with increasing hydrophobicity of the base sheet, in agreement with the Lucas-Washburn equation.	Shirazi *et al.* 2004
During film-press application of pigmented coatings, the degree of hydrophobicity of the base sheet plays no role, whereas the applied pressure at the size press nip has a dominant effect on penetration into the sheet.	Engström 2005
Wet-end sizing with AKD had a favorable effect on surface sizing with enzyme-converted starch.	Li *et al.* 2013

A likely explanation for the effects just described may lie in the different wettability characteristics of different crystal planes in cellulose (Szlek *et al.* 2022). Consequences of such differences on the wettability of regenerated cellulose, depending on the nature of the media used in its regeneration, were first reported by Yamane *et al.* (2006). Less water-wettable surfaces resulted when the cellulosic material was regenerated in the presence of a non-polar, hydrophobic medium. Such conditions favored the self-assembly of cellulose, during its phase change, such that the least water-loving crystal plane was mainly facing outwards from the surfaces. It is proposed here that a similar effect may take place during gradual evaporative drying of cellulosic materials in contact with air. The mechanism is illustrated schematically in Fig. 30.

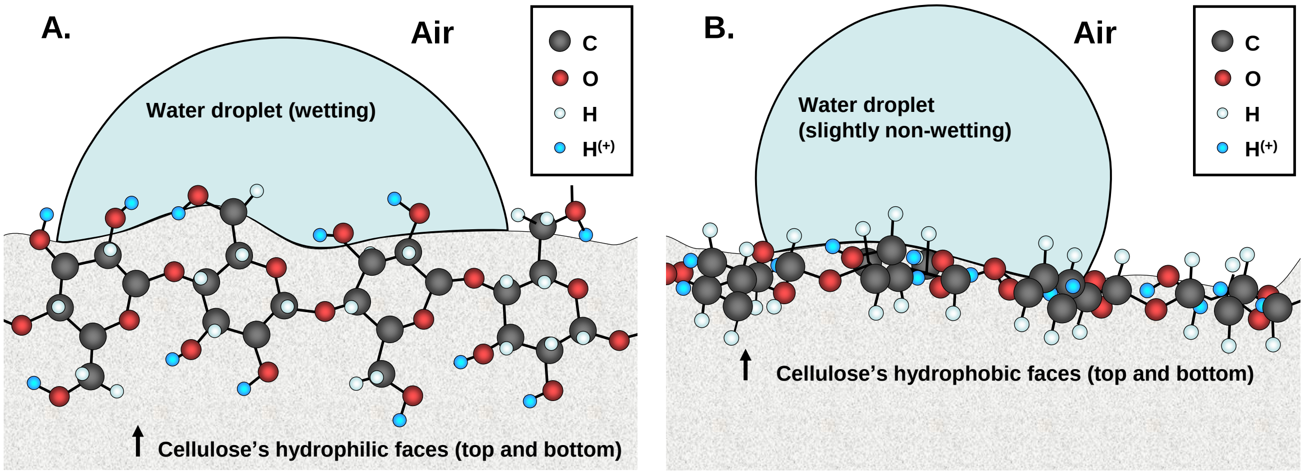


Fig. 30. Sketch to explain initial reluctance of air-dried paper to become rewetted by water. A: Non-wetting droplet on cellulose that is projecting its non-wetting crystal plane; B: Wetting droplet on cellulose that has had time to reorient so that its hydrophilic crystal planes predominantly face the aqueous phase. (The representation of atomic positions in the two planes are based on Yamane *et al.* (2006), as redrawn by the author in Szlek *et al.* (2022))

Wilson (2005) reported different trends, compared to those mentioned above. It was reported that sheets having a moisture level of 8%, which is close to the equilibrium moisture content in typical room conditions, gave good hold-up of size press starch. By contrast, very dry paper, having a 2% moisture content, tended to suck water from the applied size press formulation. Follow-up work may be needed to sort out the apparent disagreement in findings.

Uniformity of the Applied Film

Most paper products are sold on a commodity basis, such that customers can obtain almost equivalent products, meeting the same specifications, from several sources. To thrive in such a competitive environment, each supplier needs to achieve a high reputation for uniformity and reliability. A non-uniform paper surface can lead to printing defects such as print mottle and nonuniformity of intended monotone print areas. Printers can make adjustments in response to differing paper attributes, but such corrective actions require that the paper is relatively uniform over the dimensions of both space and time.

Effects related to formation uniformity

A flocculated nature of the base stock, *i.e.* nonuniform formation, has been sometimes blamed for nonuniform uptake of starch at the size press, when comparing adjacent areas on a scale of several millimeters. Such underlying nonuniformity in porosity may explain results reported by Engström *et al.* (1997), who used a film press to apply pigmented coatings. Porosity variations in those coatings were correlated with observed print mottle effects. Given the very low number of published studies in this area, future work in needed to help quantify the degree to which base sheet uniformity, including aspects such as roughness, effects due to fiber flocs, and effects due to paper density variations may be responsible for printing defects that remain after a size press operation. An expected mechanism by which non-uniform formation within the base sheet can be expected to affect the results of size press application is illustrated in Fig. 31.

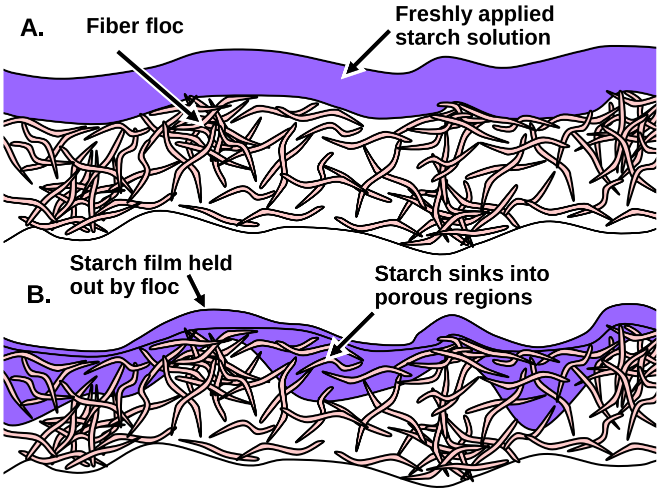


Fig. 31. Expected effects of nonuniform base sheet structure on the location and nature of a surface-applied starch film on paper. A: At the instant of application of the starch film; B: After passing through the press nip and any capillary effect

Effects related to the metering system

Various metering systems, including metering blades, wire-wound rods, and gate-roll metering systems have been widely used for size press applications, as described earlier in this article. The goal, in each case, is to spread a uniform film of controlled thickness over the surface of a size press roll. In theory, a wire-wound rod has the potential to produce fine ridges in the spread film, corresponding to the pattern of the grooves. However, no report was found indicating any such issues. On the other hand, it has been hypothesized that flow instabilities associated with rod coating may contribute to film splitting problems (Triantafillopoulos and Aidun 1990; Alonso *et al.* 2000; Roper *et al.* 2022), which will be considered next. Thus, the available literature suggests that film application is not recognized as an important source of defects on the resulting paper products.

Effects related to film splitting

Orange peel effects, related to the spitting of the starch film at the exit of the size press nip, were considered earlier in this article, and the question now is relative to the effect on the observable uniformity of the paper. Based on published descriptions, the orange peel effect manifests itself as filaments of starch that lie back down onto the paper surface after being “drawn” during the separation of the two press rolls (Roper *et al.* 1999). These features tend to become larger with increasing applied amounts of starch solution and at higher speeds, such that the filaments are unable to retract efficiently when the filaments break (Triantafillopoulos and Smith 1998; Roper *et al.* 1999; Wikström and Grön 2003; Ascanio *et al.* 2006). Roper *et al.* (1999) used Prüfbau print test strips to clearly differentiate between good and bad instances of orange peel. Scans of visible changes in intensity of light from the two groups of samples suggest that the features had sizes in the range of about 0.1 to 0.5 mm. These general findings were backed up by further micrographs shown by Wikström and Grön (2003). However, there is a puzzling aspect of the micrographs shown in the cited articles. The features show a resemblance to spherical protrusions rather than strings or ribbing, as suggested by the term “ribbing”. Thus, observers usually may have been thinking about the external surface of an orange peel, rather than the fibrous internal surface of an orange peel. Figure 32 offers a way to think about how the splitting of a starch film at the exit of a size press nip could be expected to result in this kind of surface feature.

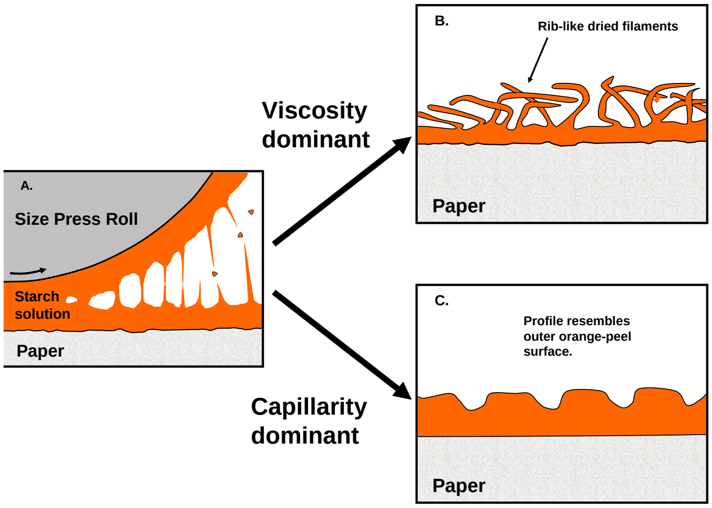


Fig. 32. Suggestion of how the retraction of broken filaments of starch solution at the exit of a size press at relatively high levels of surface application and machine speed (A) can provide a surface pattern resembling that of the interior (B) or exterior (C) surface of an orange peel

Effects related to drying practices

According to Cushing (1979), excessively rapid drying of a starch film after the size press can be expected to result in cracking and checking. No corroboration of this statement was found in the present work of reviewing the literature. As described in the earlier section dealing with size press equipment, non-contact drying methods, such as infrared heating, can be used, especially when there are sticky components, such as latex, in the formulation (Rennes 1998a,b). The idea is to remove enough water from the sheet so that the rest of the drying can be achieved using ordinary steam-heated dryer cans. Due to severe space limitations on a typical paper machine, when heating an unsupported web of paper, such devices have to remove water very quickly. There was no report, in the current review of the literature, indicating any resulting problems related to nonuniformity or cracking of the starch layer. A future study might consider whether or not the earlier statements by Cushing (1979) have important consequences, especially when drying starch films after modern size press applications.

PAPER PROPERTIES AFFECTED BY THE SIZE PRESS

Paper Strength

Strength enhancement is well known as a key contribution of starch products during paper manufacture. Starch is able to make this contribution due to the flexibility of its macromolecular chains and their ability to form hydrogen bonds among themselves and with cellulosic fibers (Hubbe 2006). Table 10 shows highlights of some publications documenting general strength improvements, stiffness increases, and surface strength enhancement achieved by size press applications. As shown, the reports cover a diverse range of compounds, some of which were used in combination with starch.

Table 10. Studies Documenting Paper Overall Strength, Stiffness, or Surface Strength Enhancement by Means of the Size Press

Key Findings Presented in the Article	**Citation**
Strength data are shown before and after surface sizing, using a variety of starch types on paper.	Rankin *et al.* 1975
The main function of size press starch is to increase paper's surface strength, whereas increases in the internal strength may be secondary in importance.	Eklund 1989
Application of size press starch to paper made with kraft fibers at a film press resulted in increased tensile strength and resistance to delamination.	Felder 1991
The size press can be used to increase surface strength of paper.	Jopson & Moore 1991
Chitosan application to the paper surface increased its surface strength, as needed for printing with tacky offset inks.	Lertsutthiwong *et al.* 2004
Starch application to paper increased the cross-directional strength properties but not the machine-directional properties. Wetting by water alone tended to hurt sheet strength. Strength gains were exhibited as increased Young's modulus.	Lipponen *et al.* 2005
Surface application of chitosan contributed to increased tensile strength, in addition to barrier properties.	Kjellgren *et al.* 2006
Surface sizing increases physical strength properties of paper and binds particles to the paper surface.	Biricik *et al.* 2011
A waterglass-starch mixture was applied to the paper surface to increase the strength of linerboard.	Peng *et al.* 2011
Waterborne epoxy resin applied at paper's surface increased both overall strength and stiffness.	Li *et al.* 2012
Tensile strength and bending stiffness of linerboard were increased by surface application of a starch-fatty acid complex.	Yan *et al.* 2012
Modified collagen was shown to be effective as a surface sizing agent for increasing tensile strength and tearing resistance.	Wang *et al.* 2013
Paper strength was increased by means of a UV-curable polyurethane surface sizing agent.	Wang *et al.* 2015a
Ultrasonically converted starch showed paper strength gains similar to those provided by starch that had been converted by other means.	Brenner *et al.* 2016
The strength and stiffness of paper was increased by size press application of a combination of starch and 3-aminopropyl-trimethoxysilane.	Ni *et al.* 2017
The review article states that starch provides general strength improvements, stiffness, and erasability, which may be related to surface strength.	Bajpai 2018
Tensile strength of paper can be increased when there is substantial penetration of surface-applied starch into the web, whereas bending stiffness is higher when the starch is held out near to the paper surface, which can be achieved by adding cationic acrylamide copolymer to the formulation.	Seo *et al.* 2020
A copolymer of polyvinyl alcohol and polyurethane was applied at the size press to strengthen specialty paper.	Liu *et al.* 2021
Cross-linked polyvinyl alcohol applied to paper's surface greatly increased paper's strength and folding resistance.	Li *et al.* 2022
Different enzymes used for conversion of starch yielded different results in terms of paper strength.	Wang *et al.* 2022

As shown in the table, a key effect of size press starch application has been to increase the stiffness of paper. Figure 33 suggests an explanation of why such a contribution of stiffness is likely to depend on optimization of the starch solution's penetration into the base paper. However, the depicted hypothetical case of complete non-penetration of the starch film is considered unlikely due to the highly porous and wettable nature of typical uncoated paper sheets.

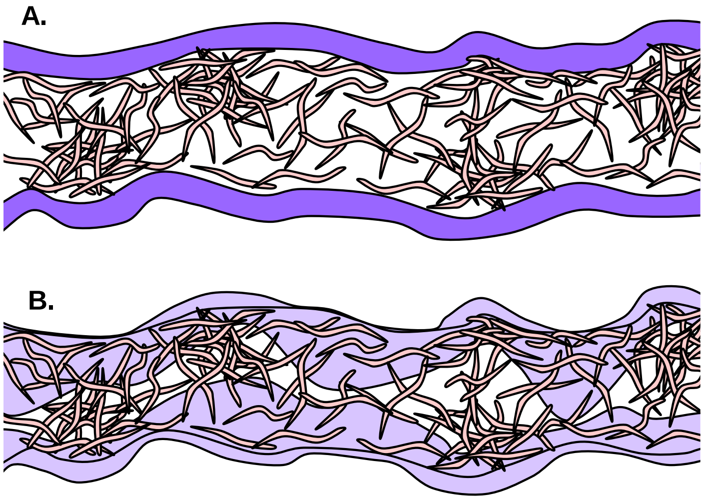


Fig. 33. Expected dependency of paper stiffness on the degree of permeation of size press starch into a paper sheet. A: Ideally high hold-out, providing maximum I-beam effect; B: extensive permeation, maximizing sheet tensile strength, *etc.*

Dust Control and Printer Contamination

Due to their relatively high content of inorganic filler, usually calcium carbonate particles, printing papers can be a source of particulate matter that can contaminate the air and cause problems with printing operations (Daniels 1976).

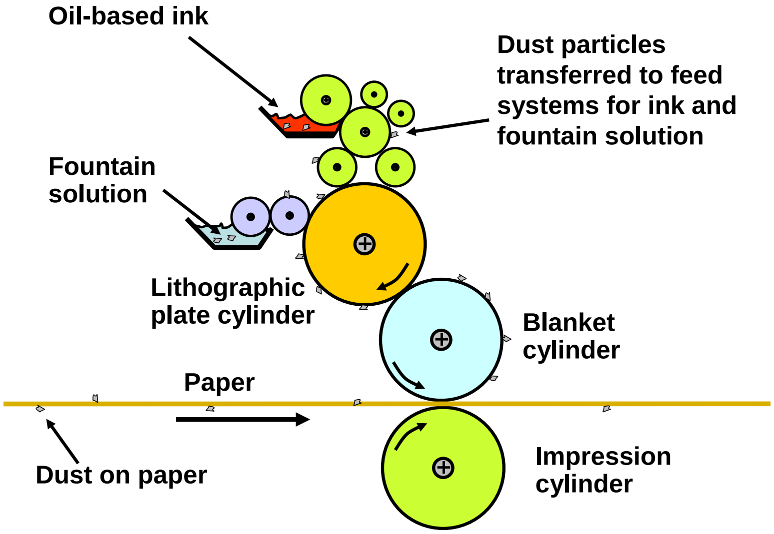


Fig. 34. Contamination of an offset printing operation, including print blanket contamination and fountain solution contamination, due to picking of dust from a paper surface

Such problems often can be reduced by the application of starch at a size press. Fineman and Hoc (1978a,b) found that application of starch with a flooded nip size press was able to reduce linting of fine paper. Significant improvements were achieved even at a relatively low application of 1.5 g/m^2. Further gains were achieved by the use of rosin to render the paper surface somewhat hydrophobic and thus resistant to the fountain solution used in offset printing. Trouve and Takala (1993) used a Taber abrasion test to evaluate dust generation from highly filled paper sheets. Adding a glyoxal crosslinker to the size press starch formulation was found to significantly reduce dusting. The improvements were attributed to increased surface strength of the paper. Song *et al.* (2010) showed that the linting propensity of paper could be decreased by applying a solution of anionic starch, reinforced with nanocellulose, to the paper surface. Figure 34 illustrates how loose particulate matter at the paper surface is likely to contaminate an offset printing operation.

Print Density and Resolution

Print density is a measure of the ability of the printed ink to reduce the amount of light, sometimes of selected wavelengths, that comes back to the eye of the observer. For instance, a pure black ideally would not diffusely reflect any incident light. Such outcomes are more likely to come closer to full achievement when the applied ink remains held out at the surface of the paper, rather than penetrating into the fiber layers. Such issues are especially important in common water-based inkjet applications in which the ink jet fluid has a low viscosity. According to Bajpai (2018), size press treatment with hydrophobic agents can contribute to such performance by decreasing the wettability of the surfaces. The needed decrease in wettability especially can be achieved by adding a hydrophobic copolymer to the size press formulation. Thus, Barker *et al.* (1992) showed improved inkjet print results when styrene acrylic copolymer was added with the size press starch. Related findings were shown by Moutinho *et al.* (2007, 2009) and by Stankovska *et al.* (2014). Again, the increased saturation of printed areas was correlated to the decreased water-wettability of paper that had been surface-sized with the inclusion of hydrophobic copolymers. Figure 35 suggests a mechanism by which such effects take place.

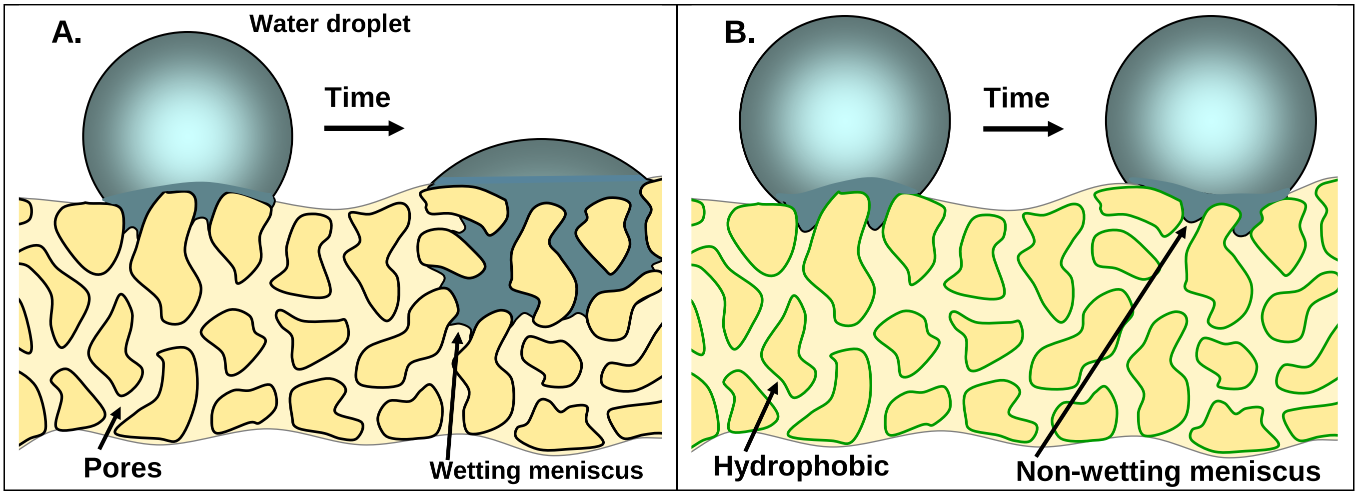


Fig. 35. Sketch showing the effected effect of hydrophobic copolymers added to size press starch in minimizing penetration of inkjet ink, thus increasing the print density, but with some danger of increased smearing in case of delayed drying. A: Hydrophilic surfaces, including within pores; B: Hydrophobic surfaces

Related benefits can be obtained by adding high surface area mineral particles to the size press formulation. Darwin *et al.* (2000), Batz-Sohn *et al.* (2009), and Zhang *et al.* (2013) achieved higher print density when using high surface area silica products in size press formulations. Zhang *et al.* (2013) found that high surface area minerals added to the size press starch solution improved the resolution of dots and lines. Stankovska *et al.* (2014) reported similar improvements when using various hydrophobic additives at the size press. The beneficial effect was attributed to the ability of such mineral particles to absorb large amounts of colorant and hold the chromophores near to the surface of the paper.

EMERGING TRENDS AND APPLICATIONS

Sometimes, when attempting to identify pivotal advances in technology, there can be an advantage to the passage of relatively large spans of time. One such change, in the context of this article, has been the replacement of most flooded nip size press installations by film presses (Eklund 1989; Tehomaa *et al.* 1992; Klass 1998). But the story clearly does not end there. Film presses have enabled further advances related to pigmented size press formulations (Zou and Vidal 2003). Either directly or as a pretreatment, film presses have potential to contribute to other paper grade developments. This section deals with publications related to such advances.

Paper Grade Extensions

Table 11 describes a variety of paper grades that have been enabled by application of size press technology, especially with the usage of film presses. As shown, these developments have been quite diverse, allowing extension of paper products into several specialty areas.

Table 11. Articles Describing Paper Grade Developments and Extensions Enabled by Film Press Applications

Article topic	**Citation**
Satinized paper from a newsprint base by means of a size press	Bergh & Svenka 1990
Improvement in paper market value due to size press treatment	Jopson & Moore 1991
Improvement of surface strength, opticals, printability, friction, *etc*.	Post 1991
Size press pigmentation for enhancement of printing papers	Turunen 1993
Starch application to increase the strength of corrugating medium	Wolf 1993
Pigmentation of wood-free and wood-containing printing grades	Rantanen & Finch 1994
Improved quality of mechanical pulp paper grades using starch	Hiorns & Sharma 1996
Separate size press applications, enabling more options	Aarnikoivu 1998
Web offset printability on newsprint paper by size press with SMA	Burri *et al.* 1998
Fluorochemical grease resistant agents added at the size press	Deisenroth *et al.* 1998
Light-weight coated offset paper quality improvement	Kogler 1998
Precoated paper using a metered size press	Arnold *et al.* 2000
Silica application by different size presses for inkjet printing	Darwin *et al.* 2000
Precoating, then top coating, for inkjet paper enhancement	Kaipf *et al.* 2000
Light-weight mechanical pulp grades for improved printing	Ahlroos & Grön 2001
Size press application with styrene acrylate for inkjet printability	Carceller & Juppo 2004
Improved inkjet printability by light size-press pigment application	Cui *et al.* 2008
Size press application of fumed silica coating for inkjet printability	Batz-Sohn *et al.* 2009
Superhydrophobic paper by means of size press application	Chen *et al.* 2017

The final item in Table 11 is interesting because the size press may offer a way to bring down the cost of achieving a remarkable effect. The term "superhydrophobic" means that a droplet of pure water placed on the surface will display a contact angle of at least 150 degrees (Song and Rojas 2013; Yun *et al.* 2023). As illustrated in Fig. 36, the effect is most often achieved by a combination of treating the surface with nanoparticles, thus creating roughness at the nano scale, in combination with a low-energy monomolecular film covering everything. As described earlier in this article, the starch film can be rendered hydrophobic by optimized treatment with a hydrophobic copolymer (Bildik Dal and Hubbe 2021). Alternatively, the hydrophobicity can be provided by a reactive sizing agent, such as alkylketene dimer (Szlek *et al.* 2022). The concept of spraying an ethanol suspension of hydrophobic nanoparticles onto the undried surface of a starch film was pioneered by Chen *et al.* (2017). Silica nanoparticles were rendered hydrophobic by treatment with hexamethyl disilazone. In this simple way, even without hydrophobic additives to the starch, the cited authors were able to obtain superhydrophobic properties that were resistant to bending and scratching of the paper.

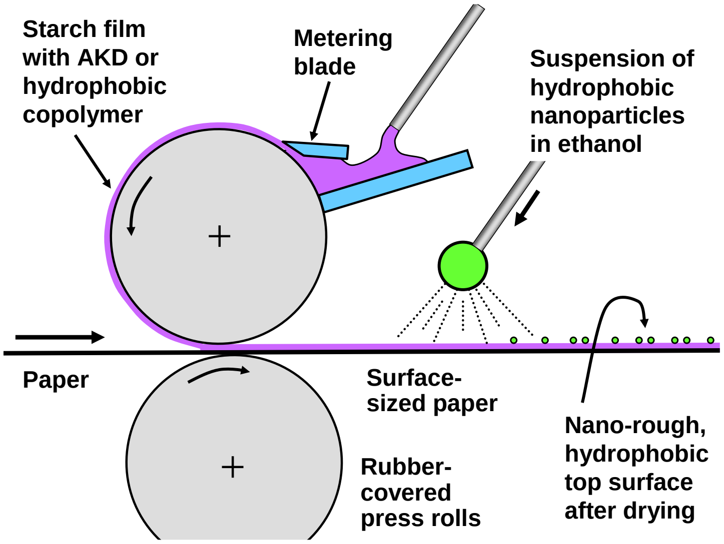


Fig. 36. Schematic illustration of how a superhydrophobic effect of a paper surface can be practically achieved by size press application

Size Press before Coating

Papermakers often need to make difficult choices between more complicated processes that make more efficient usage of materials *vs.* simpler approaches that may be easier and cheaper to implement, but possibly result in lower quality or higher costs of materials. High-end glossy paper and paperboard products are often manufactured using two successive paper coating applications. The first of these often employs relatively coarse mineral particles. Rather than developing gloss or a high degree of smoothness, the goal of the first coating layer is to fill in valleys in a rough base paper surface and to reduce the permeability of the paper in advance of the next coating application. Research has suggested that a pigmented size press application sometimes can adequately serve as a substitute for the first of two conventional coating layers (Adams 1983; Klass 1990b; Kuchinke 1993; Ryder 1998). Reports about such systems are summarized in Table 12.

Table 12. Articles Describing Usage of the Size Press as a Pre-coater

Article topic	Citation
Size press treatment with starch, carboxymethyl cellulose, styrene-maleic anhydride copolymer and reactive sizing agent increased the brightness, gloss, and pick resistance after subsequent coating.	Adams 1983
Rewetting of paper at a size press, as an independent factor, had a negative effect on paper quality after subsequent coating.	Lepoutre *et al.* 1986
Size press precoating improved coater runnability and quality.	Klass 1990b
Size press precoating improved final coated paper quality.	Kuchinke 1993
Review article promotes the installation of film presses.	Akesson 1998
Increased gloss and opacity of the final coated product.	Ryder 1998
Coating coverage achieved with a film press and important factors.	Dickson *et al.* 2002

Dickson *et al.* (2002) listed the use of high levels of clay and softer size press roll covers as important factors in maximizing coverage of base sheet roughness, in preparation for a final coating.

Mineral Particles at the Size Press

Published articles have shown that further enhancements can be achieved when minerals are added directly to the size press formulation. Many of these are highlighted in Table 13. Many of these examples show potential to improve the printing performance of certain paper grades, sometimes suggesting that they can compete against other paper grades, such as coated papers. In addition, there are opportunities to prepare specialty paper products for niche uses. Figure 37 illustrates the usage of high surface area mineral products applied at the surface of paper to increase the resolution and density of ink jet print images.

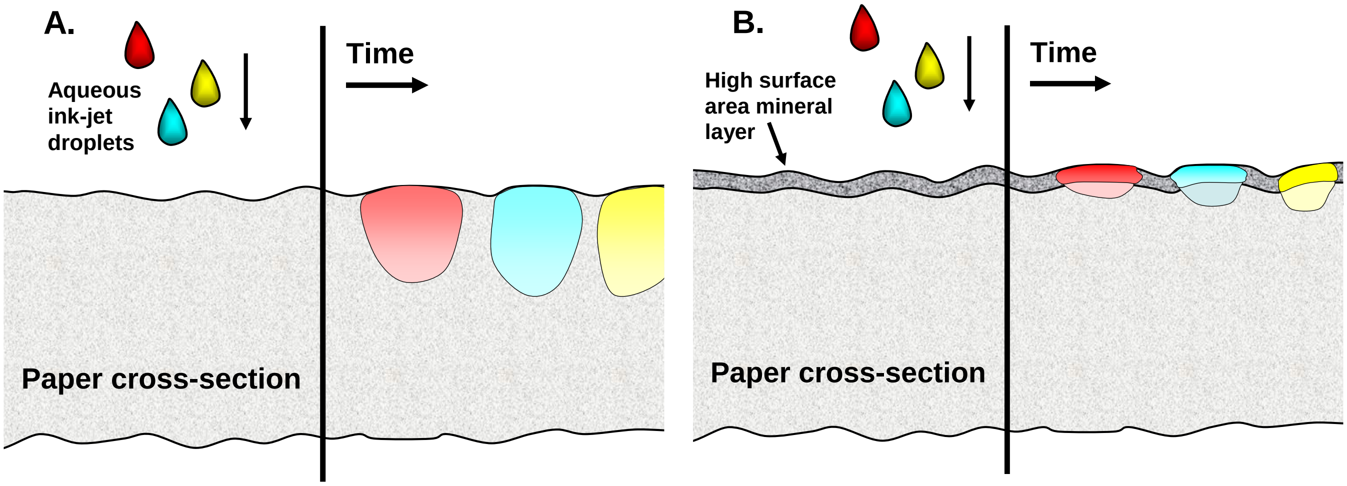


Fig. 37. Illustration of the role of high surface area mineral particles, such as fumed silica, to absorb inkjet ink, trapping the chromophores near to the paper's surface. A: Untreated paper; B: Paper with high-surface area mineral particles presumably in starch film at the paper surface

In part A of Fig. 37, it is reasonable to expect that the colorants in the inkjet fluid follow the liquid medium (often aqueous or a mixture with an alcohol) into the based sheet. In part B, one envisions the colorants adsorbing strongly onto the high-area mineral, whether or not the fluid medium penetrates further into the paper.

Table 13. Articles Describing Mineral Particle Addition at the Size Press

Article topic	Citation
Specialty minerals such as TiO_2 and precipitated silicoaluminate were able to improve the optical properties of paper that was formed from mechanical pulp and then pigmented at the size press.	Martenss 1973
Size press pigmentation can reduce sheet porosity, and specialty pigments may contribute brightness and opacity, but one should not expect important changes in smoothness or gloss.	Bailey & Brown 1990
A coating of 10% TiO_2 with 90% clay, which can be applied with a gate-roll size press, can improve the brightness of a mechanical pulp sheet, possibly allowing it to compete with products made from delignified fibers.	Johnson 1991
The combination of size press pigmentation and soft calendering improved paper quality.	Turunen 1993
Addition of highly platy smectites (swellable clays related to bentonite) was effective in limiting the penetration of size press formulation into the base sheet.	Thompson & Hutto 1997
Mineral addition to a film press formulation can improve the optical properties of the paper.	Kogler *et al.* 1998
Parallel tests with different applicators showed that a metering size press to apply a clay coating was able to achieve equivalent improvements compared to blade coatings and that the results were better than those that could be obtained with a flooded nip.	Darwin 2000
Improved coating coverage was achieved when using more clay in the formulation, which may be related to its high aspect ratio.	Dickson *et al.* 2002
Improved inkjet printing color quality was achieved when adding high surface area fumed silica to the size press formulation.	Batz-Sohn *et al.* 2009
Application of polyvinyl alcohol with silica particles increased the color density and tone reproducibility of the resulting paper.	Zhang *et al.* 2013
Clay applied at the size press showed a higher ability to remain near to the surface of the paper, which is consistent with its high aspect ratio in comparison to ground calcium carbonate particles.	Jeong & Lee 2021

Nanocellulose at the Size Press

Nanofibrillated cellulose (NFC)

Though the topic of nanocellulose has attracted a lot of attention in the field of paper science, as of yet the commercial applications have been limited. When considering the usage of NFC at the size press, there are several positive aspects. First, typical NFC products are highly compatible with starch mixtures. Both the NFC and the starch are hydrophilic, thus tending to form uniform mixtures and being capable of forming bonds with each other upon drying. Lavoine *et al.* (2014) showed that the bending stiffness of paper could be increased by 50% when NFC was added to the paper surface. Fidan *et al.* (2021) showed that inclusion of NFC in a size press formulation was able to increase tensile and burst strength values by 52% and 194%, respectively. In follow-up work, Tozluoglu and Fidan (2023) showed that a combination of cationic starch and NFC applied to the surface was able to increase the tensile strength and internal bond strength of corrugating medium.

An example of such benefits is shown in Fig. 38. Here, the researchers delignified the fibers with sodium hydroxide and sodium borohydride, followed by high-pressure microfluidization to produce NFC. The default base-sheet (corrugating medium) was compared with versions treated at the 0.5%, 1%, 2%, 3%, and 4% levels with NFC. As shown, the tensile index increased by a factor of about 1.4 and the air permeability fell to about 0.17 times its initial value as the level of nanocellulose was raised from zero to 4% (Tozluoglu and Fidan 2023).

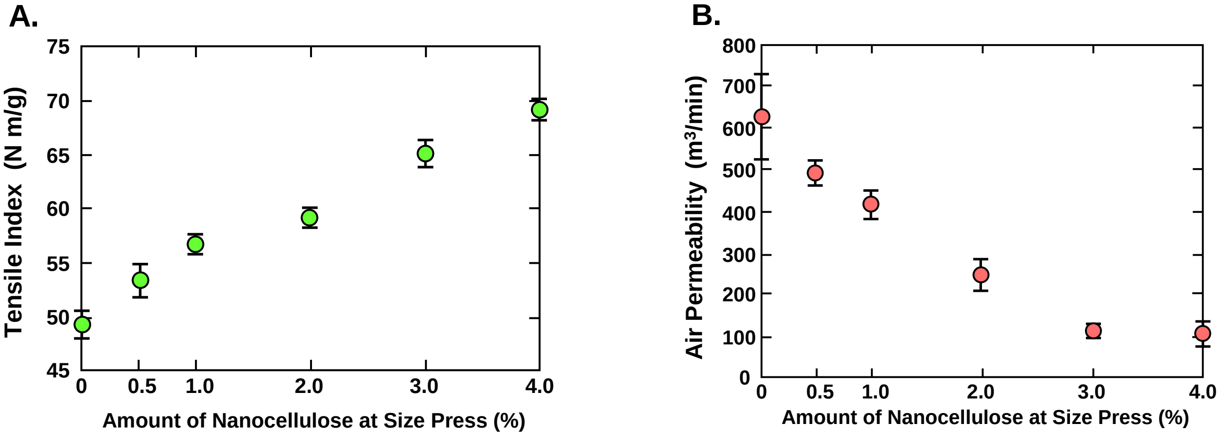


Fig. 38. Examples of paperboard strength and resistance to air permeation increases achieved by inclusion of nanocellulose at the levels shown included with 4% solids corn starch solution at the size press. A: Tensile index (N·m/g); B: Air permeability (m^3/min); Data replotted from Tozluoglu and Fidan (2023)

The most important downside of using nanocellulose at the size press is likely to be its strong contribution to viscosity. Nanofibrillated cellulose (NFC) suspensions, with or without dissolved starch in the mixture, tend to be shear-thinning (Hubbe *et al.* 2017; Li *et al.* 2020). However, one needs to bear in mind that size-press starch needs to be converted (reduced in molecular weight) to be able to run well during film application and in the press nip. Anything that adds to the viscosity of the mixture can be expected to limit the amount of solids that can be applied at a size press. For example, Lavoine *et al.* (2014) had to employ ten successive size press passes with microfibrillated cellulose suspension to reach an applied amount of 4 g/m^2.

Nanocrystalline cellulose, which is most often prepared by controlled digestion of cellulosic source material with concentrated sulfuric acid, has the potential advantage of less contribution to viscosity of the suspension. Yang *et al.* (2016) showed that addition of such crystals to a size press formulation contributed positively to paper strength, in addition to some other benefits. The term "nanocomposite" is appropriate for such systems, since the starch represents a continuous matrix phase and the nanocellulose can serve as reinforcing particles (Hubbe *et al.* 2008b). Figure 39 contrasts the typical shapes and typical viscosity-solids relationships of nanocrystalline cellulose (A) and NFC (B) suspensions (Hubbe *et al.* 2017). In addition, part C shows the viscosity of suspensions of each type of nanocellulose *vs.* solids content in aqueous solution, based on findings from a large number of publications. As shown in part C of Fig. 39, there has been a very large variability in viscosity values reported at specified solids levels of nanocellulose in aqueous suspensions. Especially in the case of cellulose nanocrystals, it had been proposed that results of such studies tend to fall into two categories, depending on whether or not the solids were in the form of a contiguous network at the time of evaluation (Hubbe *et al.* 2017). The fact that the data are able to fall neatly into two categories is tentatively attributed to the simple shape and dimensions of typical cellulose nanocrystal (CNC) suspensions.

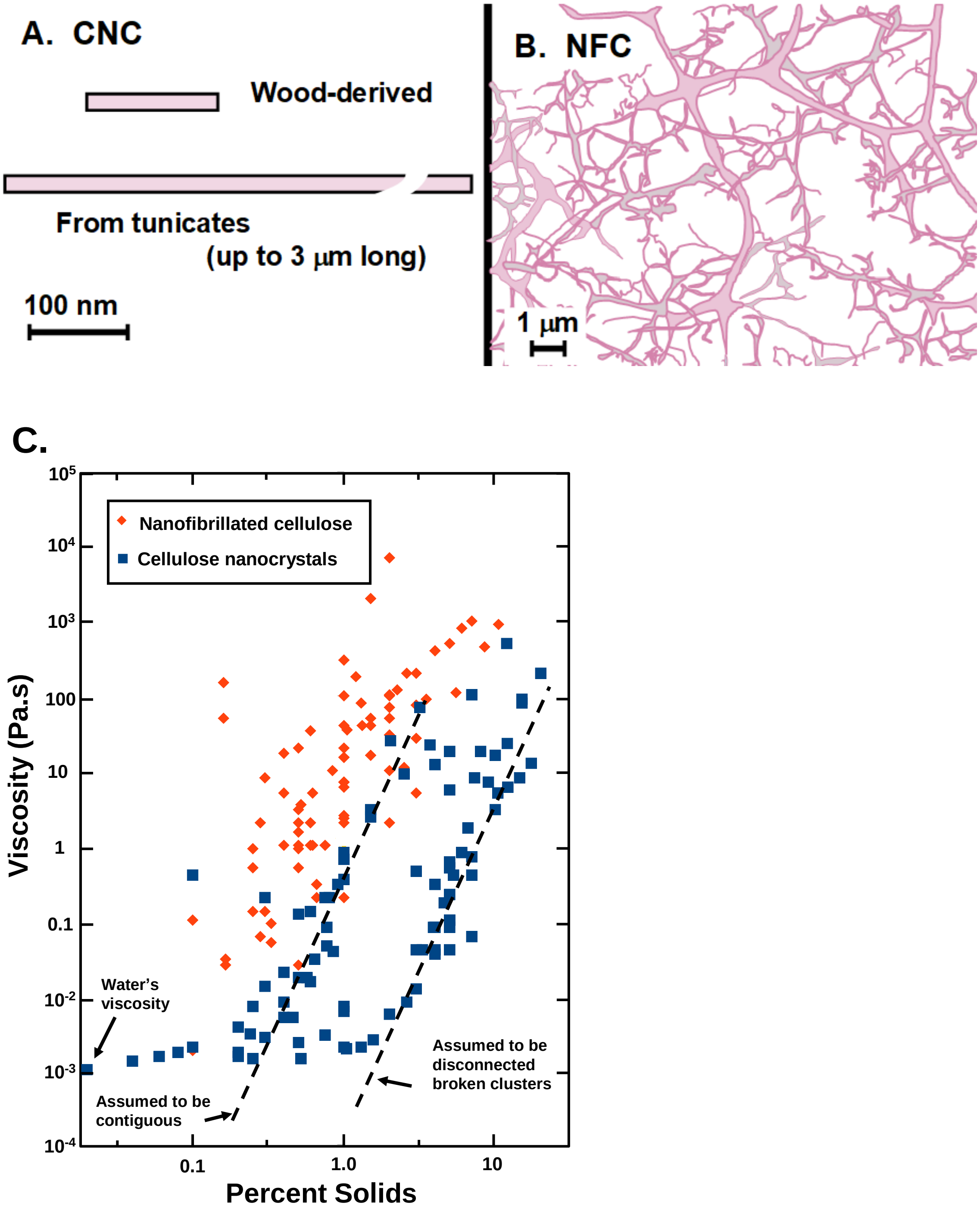


Fig. 39. Comparison of the shapes of two forms of nanocellulose and their corresponding viscosity-solids relationships (simplified from Hubbe *et al.* 2017). A: Representative size of cellulose nanocrystals; B: Representative moderately simplified traced image of nanofibrillated cellulose; C: Viscosity-solids relationships from multiple studies reviewed in the cited work

The results corresponding to nanofibrillated cellulose (NFC) in Fig. 39, part C, do not likewise fall neatly into two categories; however, there is a similarly large spread between the highest and lowest values (often by a factor of over 100) at any solids level.

Such results suggest on the one hand that the particles may form a fully linked structure, but on the other hand, such a structure may sometimes by broken down into separate clusters, separated by particle-free spaces that have viscosity similar to that of the particle-free solution (*e.g.* water).

Niche applications have been suggested that incorporate the usage of nanocellulose in combination with size press starch. For instance, Malardier-Jugroot (2015) proposed such a combination of technologies as a way to encapsulate drugs for their delivery as anti-cancer treatments. In theory, high-value applications, such as for a medical or pharmaceutical product, might have a better chance of justifying the cost of drying that is inherent in the preparation of nanocellulose-based films.

Development of Barrier Performance

For such applications as food packaging, there is much interest in barrier layers on paper items. Eco-friendly barriers have prospects for the replacement of plastics, including the polyethylene laminate films that are applied to such products as milk cartons. Table 14 highlights findings of studies related to such goals with the incorporation of size press technology.

Table 14. Articles Describing Barrier Layers Applied at the Size Press

Article topic	Citation
Based on reviewed literature, surface-applied starch tends to decrease oil permeation into paper.	Cushing 1979
By usage of platy particles such as clay or talc, it was possible to improve barrier performance compared to size press starch alone.	Reinhardt & Kramer 1996
Surface-applied chitosan decreased oil absorption by half, as did a 10% solution of polyvinyl alcohol.	Lertsutthiwong *et al.* 2004
Surface-applied chitosan provided good barrier performance against oxygen, nitrogen, carbon dioxide, air, and grease. Water resistance was decreased by the chitosan treatment.	Kjellgren *et al.* 2006
Polyvinyl alcohol applied to the paper surface decreased the absorption of castor oil, based on tests with the Cobb sizing equipment.	Gigac *et al.* 2018
Application of NFC together with starch at the paper surface decreased air permeability substantially.	Fidan *et al.* 2021

In light of the relatively few and limited studies represented in the table, a possible response might be to recommend more studies. However, it is not reasonable to expect that a typical size press formulation, which often has a starch solids content below about 18%, would be able to effectively fill and block pores within a paper base sheet. Rather, after the water has been evaporated, the previously dissolved polymeric content of a size press formulation will have retracted towards the junctions between fibers (Pan *et al.* 1995). This process will be expected to leave most of the pores at least partially open.

A possible path forward, in the direction of size-press-applied barrier layers, would be to rely upon highly platy mineral particles of optimum size (Thompson and Hutto 1997). In addition to helping to inhibit passage of the size press formulation into pores of the paper web, such platy particles also would be expected to contribute to blocking the passage of oxygen and other gas molecules through a starch-based film (Spence *et al.* 2011; Idris *et al.* 2022). Because the blocking effect is physical, rather than depending on capillary action, it is reasonable to expect that an optimized formulation can resist being driven into the pores of paper due to the pressure exerted in the size press nip. Kimpimäki and Rennes (2000) and Kimpimäki (2001) described use of a "sealing chemical" to achieve similar effects. A possible version of this approach is illustrated in Fig. 40.

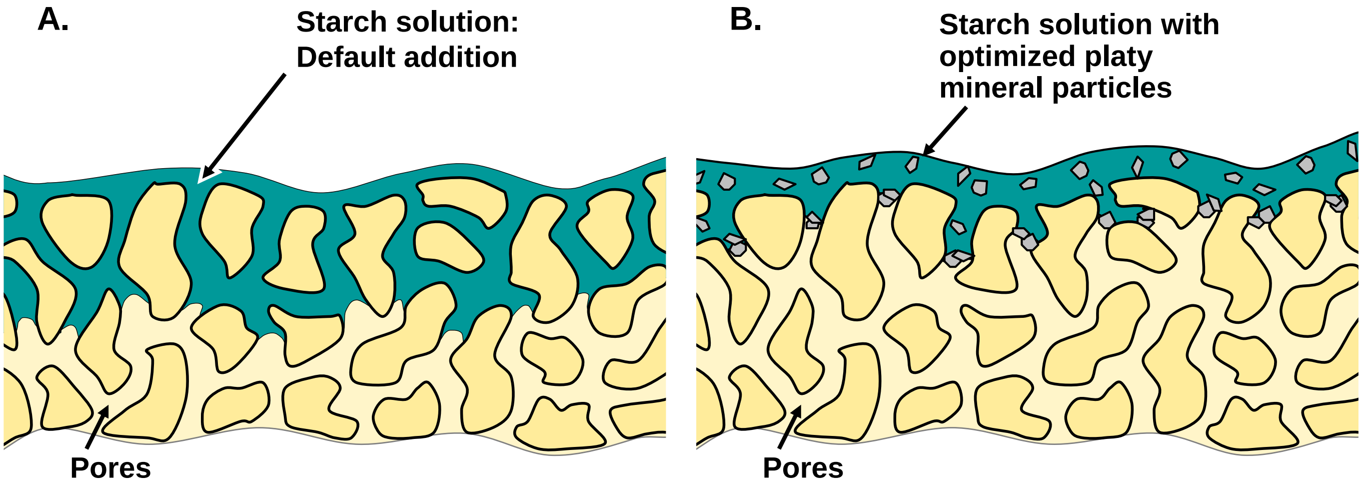


Fig. 40. Depiction of a possible system that combines starch solution and an optimized highly platy mineral particle with the goal of holding out the size press formulation need to the paper surface. A: Hypothetical default starch solution; B. Expected consequences of platy particles large enough to block pores within the paper web

In addition to the pore-blocking approach illustrated in Fig. 40, some additional measures to improve the barrier performance of paper-based items, often by means of coatings, have been reviewed. For instance, alternative measures to achieve water repellency in eco-friendly barrier layers for food packaging have been considered (Szlek *et al.* 2022). In addition to the hydrophobic copolymers that are often used in size press formulation (Bildik Dal and Hubbe 2021), one may also consider the use of alkylketene dimer (AKD), as well as trialkoxysilane formulations (Szlek *et al.* 2022).

Though it has been shown that excellent barrier performance relative to both oxygen and grease can be achieved under dry conditions with dense NFC layers (Aulin *et al.* 2010; Ferrer *et al.* 2016; Szlek *et al.* 2022), this may be difficult to achieve *via* size press technologies. The reason is related to the expected moisture uptake and swelling that can be expected in many end-use environments. In addition, NFC formulations can have very high coefficients of viscosity, even when the nanocellulose is present at very low solids levels, *e.g.* 2 to 5% (see Fig. 39, part C). The highest resistance to oxygen is often found when using nanocellulose alone (Aulin *et al.* 2010), which does not represent a typical size press formulation. Nevertheless, in light of the positive contributions to strength and reduced air permeability (Tozluoglu and Fidan 2023, see Fig. 38), the use of NFC at the size press still merits further study.

Alternatives to the Size Press

As has been shown in this article, based on many cited publications, the size press can be used as a means of achieving many important goals for papermakers. But the size press is not necessarily the best device for all such goals. A key problem associated with size press usage, even when using film-press technology with increased solids contents of the formulation, is that the paper becomes at least partially rewetted, and energy must be expended to redry the paper. Gray and Rende (2005) estimated that the moisture content of the paper increases to about 34% in a typical size press operation, in comparison to about 6% of moisture in an air-dry sheet of paper at typical humidity levels. Three promising alternatives, to deal with such issues in certain paper products, have been considered in other articles, and these are considered below.

Spraying starch at the Fourdrinier

When overall paper strength is the issue, rather than surface strength or printing issues, a cheaper approach, compared to using a size press, may be to spray uncooked starch onto a wet Fourdrinier web, usually at a position after the first suction box (Price and Hubbe 2021). The idea is to allow the starch grains to at last partly swell and gelatinize during the course of drying the paper, thus contributing to inter-fiber bonding. Because such an application takes place during the forming process, rewetting of the paper web is not involved. As noted in the cited review article, spraying starch onto the wet web of paper often is easiest to justify when producing paperboard grades, *e.g.*, linerboard prepared from recycled fibers.

Wet-end strategies aimed at large gains in paper strength

Some competing strategies aimed at achieving relatively large strength increases, possibly matching what can be achieved by size press starch or other soluble polymer addition to the paper surface, are based on multi-component polymer additions at the wet end. Brouwer (1997) claimed, for example, that a combination of anionic wet-end starch added sequentially after a cationic additive could make that possible. The usual level of starch addition at the wet end often becomes ineffective at levels above about 1.5% (Brouwer 1997; Glittenberg *et al.* 2004), which can be attributed to limited adsorption capacity of the fiber surfaces. In principle, this barrier can be overcome by the sequential additive of cationic and then anionic components (Hubbe 2005, 2006, 2014). Potential downsides of such an approach can include the excessive cost associated with high amounts of treatment and potential contamination of the wetted surfaces of the papermaking equipment (Heermann *et al.* 2006). In addition, very high levels of starch, especially when it has been modified with phosphate groups, can be expected to contribute to biological slime problems.

Conventional or specialized mineral coatings

The book edited by Paltakari (2009), which has been cited frequently in this article due to its coverage of size press topics, also covers the topic of aqueous coating technology for papermaking. True aqueous coatings are applied, usually with a blade, directly onto the surface of paper. Such operations have the potential to far exceed many of the outcomes that can be achieved when relying upon a size press, in which a key distinguishing feature is the size press nip between two rolls. The solids contents of typical water-based coating formulations are often in a solids range of 30 to 65% (Klass 1998). Starch products are widely used as binders in aqueous coating formulations (Li *et al.* 2019), which can be counted as a similarity to the size press. But just as often, coating formulations can rely upon latex products as their primary binder component. When a coating formulation is spread onto the paper surface, usually by means of a blade coater, the proportion of water is usually at least a factor of two lower than in a size-press operation. Furthermore, the higher viscosity of such a formulation favors its remaining on the surface of the web, rather than substantially rewetting the base paper. Aqueous coating operations appear to be particularly well suited when the goal is to achieve a glossy and smooth surface for high-end printing. On the other hand, such coated layers will not generally contribute to overall product strength or resistance to delamination.

CONCLUDING STATEMENTS

In summary, the papermaker gets to select from among more than one class of methods and devices when the goal is to add starch to the paper. The size press appears to fill the needs of papermakers very well in the case of printing papers, and sometimes in other grades of paper where there is a need for surface strength and stiffness. The flexibility in being able to add mineral particles, colorants, hydrophobic agents, and even nanocellulose, *etc.*, mean that tomorrow's product development teams for paper companies will likely come up with additional favorable uses of size-press equipment. On the other hand, issues arising from film splitting, such as misting and orange peel effects, will likely cause some developers to favor other options, such as blade coatings, depending on the end product goals.

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