Starch alternatives for improved strength, retention, and sizing

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ABSTRACT: Cationic potato starch is compared with the papermaking properties of the wet-end starches cationic cornstarches and waxy cornstarches. The amphoteric cationic potato starches show improved performance in alkaline papermaking in North America and Europe with respect to drainage, retention, strength development, and sizing efficiency.

KEYWORDS: Cationic compounds, corn starch, mechanical properties, potato starch, retention, sizing, wet end additives.

North American papermakers can choose from a wide range of cationic wet-end starches: corn- and waxy corn-based products, imported or U.S. potato starches, as well as amphoteric starches. However, today's moderate economic situation is prompting paper mills to bypass expensive starch in favor of more cost-effective materials.

Cornstarch was the first cationic starch to appear on the market simply because normal dent corn is the most abundant starch source. These early cationic starches had tertiary amine groups that are cationic only at acidic pH values. The addition of a stable cationic charge also at neutral and basic pH values required the development of quaternary ammonium groupings.

In Europe, where alkaline papermaking originated, commercial evidence has accumulated to show that cationic potato starches give better total retention and sizing development than cationic corn tarches. North American papermakers are taking notice.

As American producers became aware of the potential for cationic potato starch, their reaction was threefold:

1. Produce cationic potato starch from food processing by-products
2. Create the so-called amphoteric starches by chemical introduction of phosphate groups into cationic corn, tapioca, or waxy cornstarches
3. Promote cationic waxy cornstarches.

Among the three possibilities, cationic waxy cornstarches seem to be the most attractive one for American papermakers.

For this reason, Cerestar has compared cationic waxy corn and cationic potato starch to help papermakers obtain the knowledge required to make the right decision for a specific paper mill.

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Starch properties

Waxy cornstarch

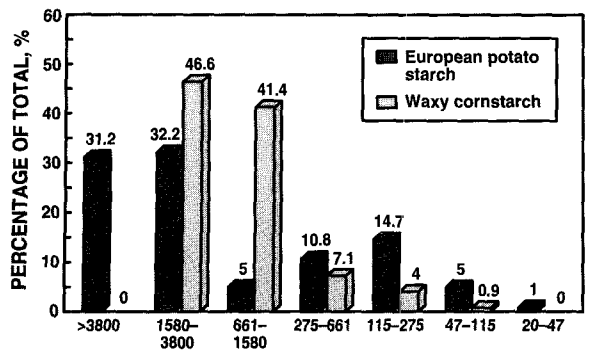
Waxy cornstarch is derived from a special breed of corn *(Zea mays)*. Its peculiarity is the complete absence of the linear starch fraction (amylose) so that it consists of > 99% of the branched amylopectin molecules. Some papers report *(1–3)* that amylopectin gives better strength improvements, whereas others doubt it *(4, 5)*.

But there is no doubt that the affinity of the short chain for cellulose is much higher than for amylopectin *(1, 6–7)*. Thus, compared with waxy cornstarch, more potato starch is adsorbed onto the fibers. In exact figures, this value is 14 against 5 mg/g *(8)*. Obviously, the more starch there is on the fiber, the more strength it can give.

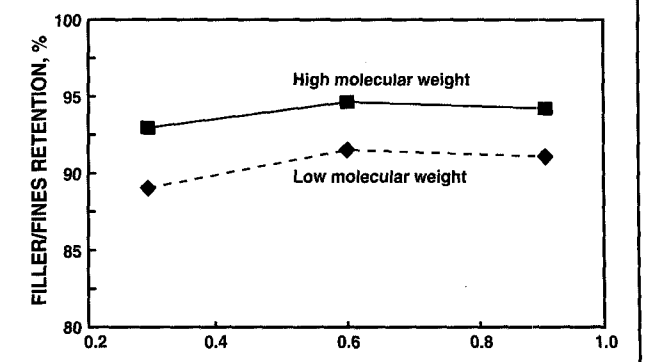
Potato starch

The amylopectin fraction of all starches has a much higher molecular weight (10^6–10^8) than the amylose fraction (10^4–10^5). This leads some to conclude that a 100% amylopectin waxy starch must automatically have a higher molecular weight than potato starch. However, the opposite is true, as is shown in **Fig. 1**. The European potato starch, for example, has 31% of its weight at molecular weights above 3.8 million Daltons, whereas the corresponding value for waxy cornstarch is zero.

1. Molecular weight distribution of potato and waxy cornstarch



2. Comparison of cationic potato starches with different molecular weight distributions—influence on total retention



Cationic potato starch

Another important difference between cationic potato starch and cationic waxy cornstarch is the number of anionic phosphate groupings that are naturally present only in potato starch. Upon cationization of the anionic native potato starch, an amphoteric starch is obtained in one step.

This amphoteric starch more effectively forms extended three-dimensional networks, by self-association of the anionic and cationic groupings, than does simple cationic starch where the cationic groups are repulsing each other.

This leads us to the importance of the two properties of starch: molecular weight and amphoteric character.

I. Mill trials in a U.S. fine paper mill — grade averages

	Starch type	*Retention, %*	*Starch dosage, lb/ton*
PM 2:	Waxy corn	97.1	21.6
Grade A	Potato	98.3	18.9
Grade B	Waxy corn	81.2	17.5
	Potato	86.5	16.3
Grade C	Waxy corn	82.1	27.9
	Potato	86.5	19.1
PM 3:			
Grade D	Waxy corn	94.4	18.9
	Potato	96.2	15.5

Total retention and strength properties

It has been shown, in numerous laboratory and machine trials in Europe, that a starch grade having a higher molecular weight is more efficient with regard to retention and strength. For example, bridging mechanisms during flocculation show that a more extended molecule can form bridges between particles over larger distances. This effect is enhanced when potato starches are used, as their amphoteric nature encourages self-association and buildup of three-dimensional networks.

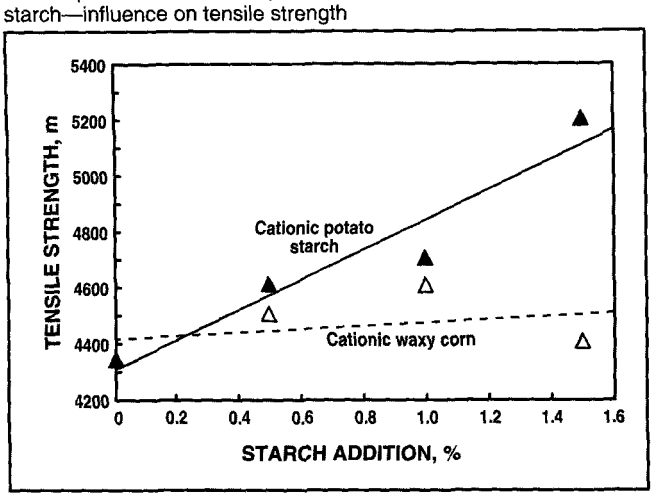
To prove the importance of molecular weight, we compared an undegraded cationic potato starch (Potato Starch A: 200 mPa·s, 3% solids, 50°C) and the same starch after reduction of its molecular weight by slight acid thinning (Potato Starch B: 200 mPa·s, 10% solids, 50°C).

Figure 2 shows the total retention for a neutral woodfree system. In this laboratory study, total retention was 5–8% higher for the higher molecular weight Potato Starch A throughout all addition levels.

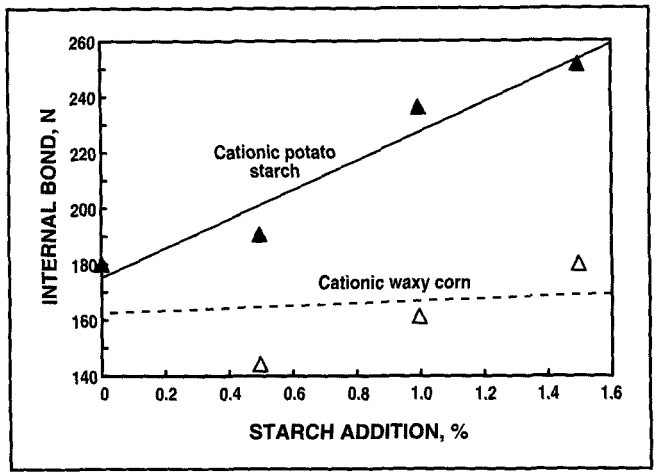
This was confirmed in comparison to waxy corn during a mill trial on a North American fine paper machine. **Table I** shows that, for both machines and different grades, the total retention was higher at a lower dosage level of cationic potato starch than with cationic waxy cornstarch. The net result was significant—up to 5% better total retention at up to 8 lb/ton less starch dosage.

Also, with respect to strength development, the use of a high molecular weight wet-end starch is to be recommended. **Figures 3 through 5** show the strength developments of wood-containing uncoated printing paper with starch addition. In this example, cationic potato starch with a degree of substitution of 0.035 is compared to a cationic waxy cornstarch with a comparable cationic substitution. As Fig. 3 shows, tensile strength is at least 100 m higher for the cationic potato starch, compared to the waxy cornstarch. Starch dosages of over 1% lead to steadily increasing values.

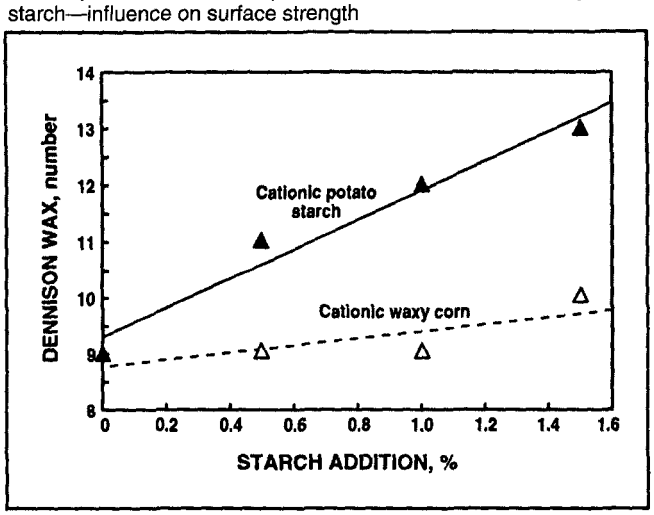
3. Comparison of cationic potato starch with cationic waxy cornstarch—influence on tensile strength



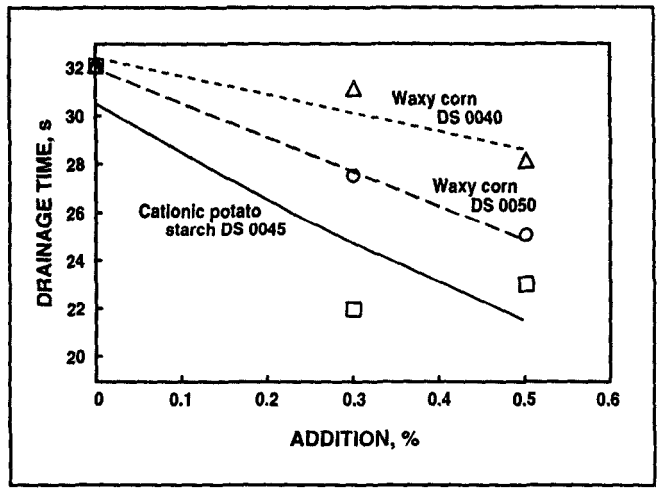
4. Comparison of cationic potato starch with cationic waxy cornstarch—influence on internal bond



5. Comparison of cationic potato starch with cationic waxy cornstarch—influence on surface strength



6. AKD-sized highly PCC-filled papers—comparison of drainage



While it was not possible to incease the internal bond by using waxy cornstarch, a 33% increase was achieved with cationic potato starch (Fig. 4). However, the increase in surface strength was most important to this North American customer (Fig. 5).

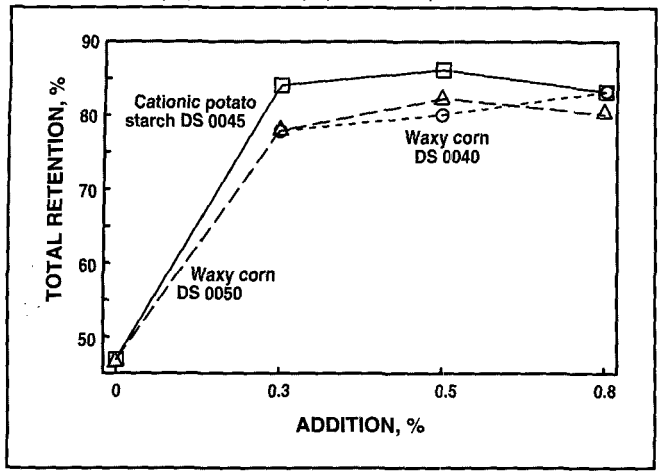
The five examples depicted in Figs. 2 through 5 clearly demonstrate that cationic waxy cornstarches do not develop the total retention and strength that cationic potato starches can. It remains to be seen whether these effects are due more to the higher molecular weight of cationic potato starch or to its amphoteric nature.

Neutral sizing

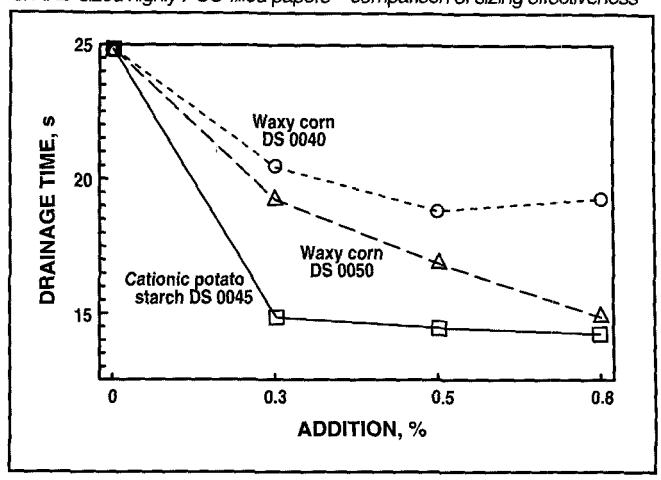
Recent published literature indicates that cationic waxy cornstarches should have superior effectivness, with respect to sizing development, in neutral sized wood-free systems. However, European papermakers use predominantly cationic potato starches in alkaline papermaking, due to the superior retentions achieved both for fillers/fines and synthetic sizing agents like AKD and ASA. Cationic potato starches give synergistic effects when used in conjunction with highly efficient dual retention systems and for strength development. European papermakers refer to the "triple" system to emphasize the important role that this type of cationic starch plays in this context. They have also tried both corn- and waxy corn-based products, but they always go back to what gives them highest cost/efficiency ratio, and that is cationic potato starch in 87% of the cases.

Nevertheless, neutral papermaking can be different in North America. Filler levels are lower and more precipitated calcium carbonate (PCC) is used. To determine if potato-based starches could provide similar results, a series of trials was conducted in Cerestar's R & D Center in Vilvoorde, Belgium, to compare a cationic potato starch with a degree of substitution (DS) of 0.045 to cationic waxy cornstarches modified to degrees of substitution of 0.04 and 0.05, respectively.

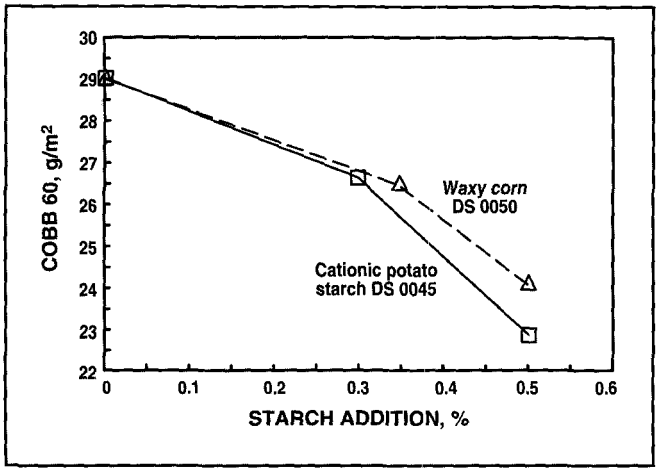
7. AKD-sized highly PCC-filled papers—comparison of total retention



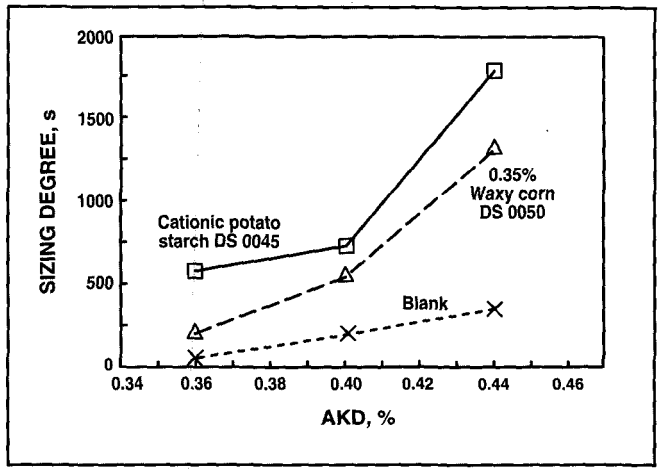
8. AKD-sized highly PCC-filled papers—comparison of sizing effectiveness



9. AKD-sized (0.44% AKD) highly PCC-filled papers—sizing effectiveness at reduced AKD dosage



10. AKD-sized highly PCC-filled papers—savings of AKD at fixed starch dosage



These cationic waxy starches showed improved performance compared to most industrially made waxy starches.

From a paper stock filled with 15% PCC, a series of laboratory sheets were prepared adding variable amounts of AKD size (Hercon 70), starch types, and starch levels.

Drainage

With regard to drainage improvement, the cationic potato starch clearly outperformed both types of cationic waxy cornstarches (**Fig. 6**) by shortening the time necessary to collect 800 mL of Shopper-Riegler filtrate out of 1000 mL stock of 0.4% consistency (at closed central opening of the Shopper-Riegler device).

The influence of the cationic DS of the waxy starches upon drainage time is clear: the higher the degree of cationic substitution, the faster the drainage. This means that flocs become more compact or hard flocculated with a higher degree of substitution and provide easier water release. However, potato starches offer faster drainage than cationic waxy cornstarches at any DS level.

Although cationic potato starch leads to better drainage behavior, strength properties are improved (as shown in the previous section) and, as is shown hereunder, sizing development is also better. This suggests that stock flocculation is different for cationic potato and waxy maize starches. The evidence is cationic potato starch's formation of microflocs rather than of harder, bigger flocs.

Total retention

In the given stock system, the advantage of cationic potato starches over both cationic waxy cornstarches is about 4–5% absolute at the normal levels of substitution (**Fig. 7**).

Sizing

At a given addition of sizing agent, the resulting sizing effect is dependent on size retention, distribution of size on the long fibers, and the regularity of sheet formation. **Figure 8** shows that cationic potato starch has almost reached its maximum effect at a starch addition level of only 0.3%, whereas 0.8% of the highest DS of cationic waxy cornstarch is needed to achieve the same low Cobb 60 level. This advan-

tage of cationic potato starch is also evident in weaker sized systems (**Fig. 9**).

If the starch dosage remains constant, more than 10% of AKD size can be saved when cationic starch is used instead of a cationic waxy cornstarch with a DS of 0.05, with an additional saving of 15% in starch dosage (**Fig. 10**).

Conclusion

Good microflocculation and formation are the key elements for both sheet strength and sizing development. We have seen how the type of starch influences these sheet properties, as well as retention and drainage.

It is evident that cationic potato starches show improved performance in alkaline papermaking in North America and Europe, with respect to drainage, retention, strength development, and sizing efficiency, when compared to cationic waxy cornstarches.

The reasons for the observed advantages of cationic potato starch are linked to the primary differences in composition and structure between the two starches:

- Cationic potato starch is amphoteric by nature, i.e., every molecule contains negatively charged phosphate groups. These groups allow for the buildup of extended molecular networks that contribute to improved retention through bridging mechanisms.
- The molecular weight of potato starch is higher than that of waxy cornstarch, resulting in higher bonding strength.

It is too simplistic to say that 99% amylopectin (as in waxy cornstarch) is better than 79% (as in potato starch) without taking into account the differences in the amylopectin structure of the two starch sources. TJ

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