

Control of wet-end Chemistry by Organic Polymers : Part X : Cationic starch as wet-end Additive*

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ABSTRACT: *Cationic starch prepared in the laboratory from tapioca starch was applied to cotton linter pulp in order to evaluate its efficacy in development of improved drystrength of the paper and also in improvement of retention of fillers. The cationic starch has been found to be capable of improving the drystrength of the paper and also in maintaining good drystrength even in presence of 40-50% filler added to the pulp. Maximum retention of filler was achieved at about 2% addition level.*

INTRODUCTION

Few papers are made from cellulose fibres alone-most contain other materials, which are added during preparation of the fibres or later to the paper webs either in drying section of the machine or during a separate off machine operation. The purpose of chemical additive is to improve a property of the paper or paperboard which is otherwise deficient.

The use of wet-end additives to improve strength of paper is as old as paper making itself. The development of strength in paper by increased beating has several disadvantages over and above it being energy consuming. Longer beating time causes the paper to shrink more on drying and to become dense, translucent, less compressible and less oil-receptive which is not desirable in a paper for printing. Therefore ways are sought to develop strength with a minimum of beating. One of the most important multipurpose additives utilised for papermaking is starch.

It has been known for a long time that wet-end starch improves drystrength, especially interfibre bonding in the sheet. Retention of regular starch (slightly anionic) is below 40%¹. Great improvements were achieved by the introduction of cationic starch strength

aids in the mid sixties. Cationic starch, because of their attraction to the anionic cellulose are virtually 100% retained on the pulps at the levels of addition usually found (0.2 to 2% on the fibre)². The strongly adsorbed cationic starch is not removed from the fibre by the usual paper making processes and repulping. Thus it is a very effective agent and does not contribute to pollution in the papermaking process.

In previous publications on this series³⁻¹¹ we have reported the preparation, properties and uses of acrylamide polymers as wet-end additives. In this paper we are reporting the wet-end behaviour of cationic starch with particular reference to improvements of dry strength and retention of fillers.

Fillers are highly desirable in printing papers, where they increase opacity and improve the printing properties. The relative price trends of fibres and fillers also tend to favour an increased use of fillers. While the optical and printing properties of the paper are improved by a higher filler load, the strength properties are,

* Part IX of this series was published in *Cellulose Chem. & Technology* (1989), 23 (6), 771-779.
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however, severely impaired. One way to improve the strength properties is to enhance the internal bonding of the sheet by the use of wet-end additives such as cationic starch.

Although use of cationic starch for development of drystrength and retention of fillers is known and a number of publications¹²⁻¹⁶ are also available on the subject, it may be observed that the results vary widely perhaps due to variations of the source of starch and method of conversion of starch to the cationic form. It is, therefore, felt that a systematic investigation of the effects of wet - end starch in papermaking is of paramount importance. The objective of the present investigation is, therefore, to illustrate strength improvement of the paper that can be obtained by incorporation of different amount of a cationic starch in presence of fillers.

EXPERIMENTAL

Materials

The pulps used in the experiments were commercially available bleached cotton linter pulp supplied in dry tap form. After disintegration the pulps were beaten to about 320 ml. CSF in a valley beater.

The cationic starch (CS) used in this investigation was prepared in the laboratory from tapioca starch (supplied by Kemphasol, Bombay), by treatment with 2 - 3 epoxypropyltrimethyl ammonium chloride in alkaline medium. The degree of substitution (DS) of the starch was 0.025. Stock solutions of this CS was made by dissolving 1 gm in 1000 ml deionized distilled water with magnetic stirring for 12 hours. Pregelatinization may be necessary for making the CS soluble and the solution used were always fresh and stored for not more than 48 hours.

The clay used was a common filler grade type. In case of calcium carbonate used as filler laboratory Reagent Grade (Sarabhai Merk, Bombay, 98%) was used. The clay slurries were dispersed with the aid of 0.3% Sodium hexametaphosphate. The filler content in the sheet is always expressed as the mass fraction of the mass of the sheet.

Methods

After the pulp had been mixed with the filler the mixture was diluted with tap water to a stock consistency of 3 gl⁻¹. The pH of the stock was 7.5, unless

otherwise stated, and was not further adjusted. The sheet was formed with a nominal grammage of 60 gm² on a standard handsheet former. The sheets were then pressed in a laboratory press and dried in vacuum.

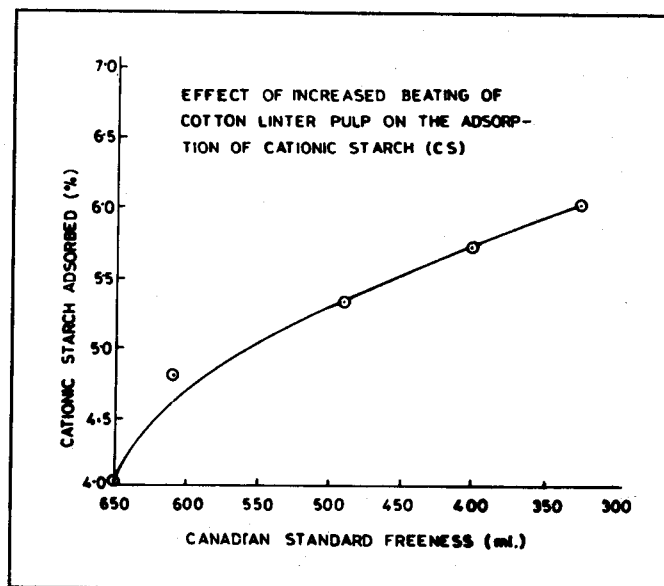
Average strength values were obtained from a total of 10 tensile tests on each sheet. The tests were carried out in a conventional tester, the rate of elongation was 0.16 mmS⁻¹ using 100 mm long strips.

The nitrogen content of the starch was determined, after thorough washing of the ungelatinized starch with deionized distilled water, by kjeldahl analysis.

Adsorption of cationic starch to cellulose fibre was evaluated by adding an excess of the starch to 0.5% consistency sample of pulp, centrifuging the fibres from the mixture. The excess amount of starch left unadsorbed by the pulp was determined colorimetrically using phenol and sulphuric acid¹⁷.

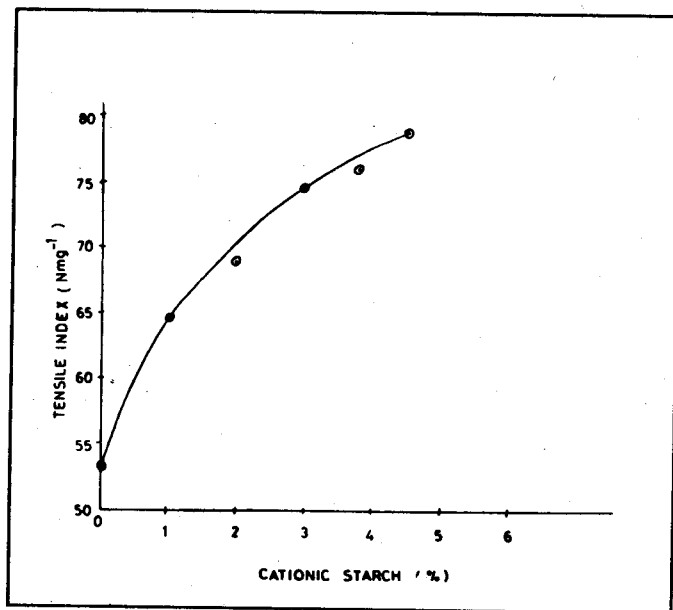
RESULTS AND DISCUSSION

The dry pulp was soaked in measured quantity of deionized distilled water for about six hours. It was then beaten in a valley beater. As the beating of the pulp progressed, a definite quantity of the pulp was withdrawn from the beater and the Canadian Standard Freeness (CSF) of the pulp was measured as usual. Another portion of the pulp was treated with cationic starch and its adsorption determined as stated above. These operations were continued till the freeness of the pulp reached 320 ml CSF. The adsorption value of the cationic starch are plotted against the freeness of the pulp (Fig. 1).



It can be seen from the figure that the adsorption of cationic starch increases with the decrease of freeness of the pulp. At about 300 ml CSF the adsorption is about 6.0% whereas adsorption at 650 ml CSF is below 4%. This is natural, because as beating progresses more and more sites for adsorption become available.

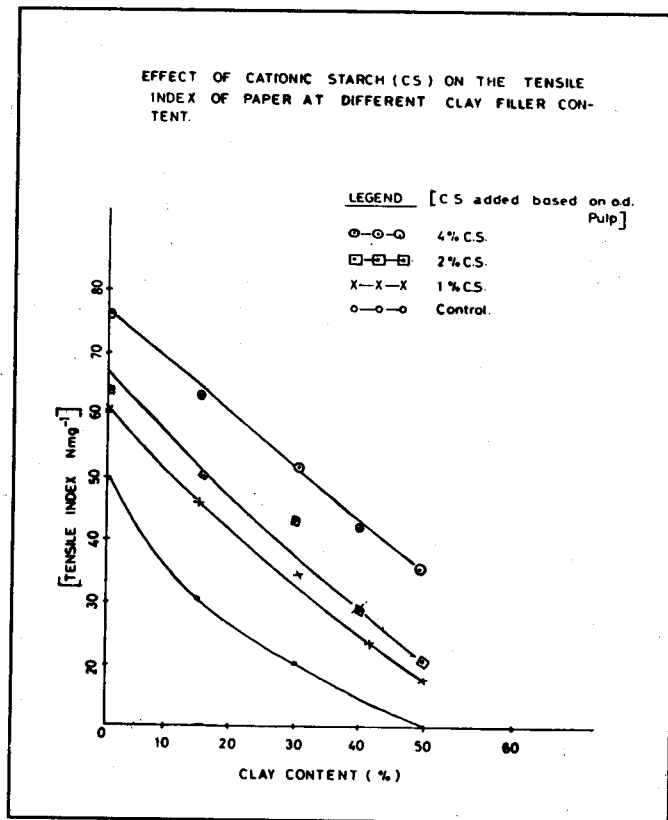
The pulp beaten to 370 ml CSF was then treated with different amounts of cationic starch. For each treatment at least ten sheets were prepared each with 60 gm². After drying and conditioning as per specification, the tensile index of each paper was determined and the average value of the tensile index (Nmg⁻¹) is plotted against percentage of cationic starch added based on o.d. pulp weight (Fig. 2).



The tensile index increases with increased concentration of cationic starch on the pulp. Since about 5% cationic starch is adsorbed 100% on the pulp (Fig. 1), addition of cationic starch upto 5% was made and it was found that tensile index jumps from 50 Nmg⁻¹ to about 78.5 Nmg⁻¹ (Fig.2).

A number of sheets were made from the stock beaten to about 370 mlCSF adding different amounts of clay filler and cationic starch. The filler content was varied from 0 to 50% followed by addition of cationic starch from 0 to 4%. It is reported that 4% cationic starch can be irreversibly adsorbed on the pulp and the bond forces are also strong enough to withstand processing and reuse¹⁸. Higher percentage of cationic starch is not effective without use of an anionic polymer. The

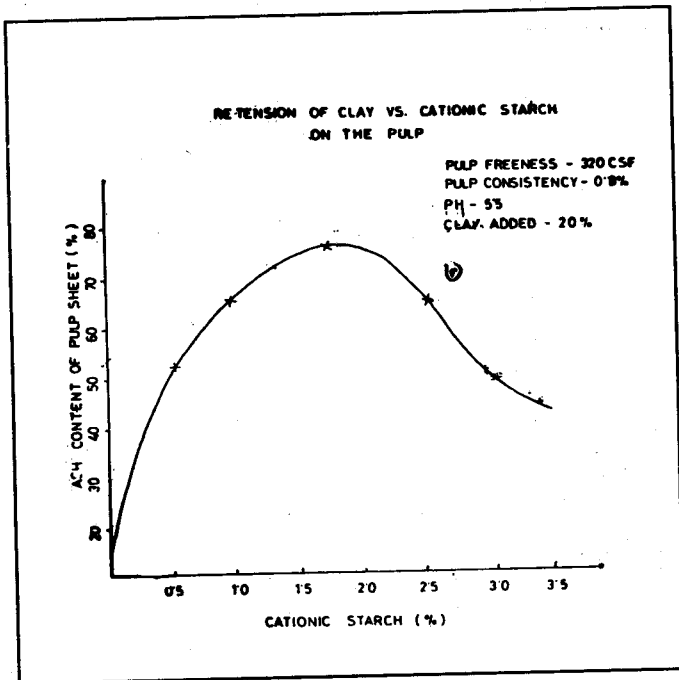
results are shown in Fig. 3. It can be seen from the figure that as the addition of clay content increases in the paper without addition of any cationic starch the tensile index decreases from about 50 Nmg⁻¹ for a blank sheet with no filler to about 10 Nmg⁻¹ when it contained 50% filler.



Comparison of Fig. 2 and Fig. 3 reveals that the tensile index of the paper is drastically lowered when filler content is increased in the pulp. In absence of cationic starch the strength goes down from 53 Nmg⁻¹ to less than 10 Nmg⁻¹ with the addition of 50% clay filler in the pulp i.e. a lowering of about 80% of the strength. Without any filler but addition of 5% cationic starch the tensile index is around 80 Nmg⁻¹ but with 50% filler added to the pulp the tensile index is just half. The tensile index of the paper with 40% filler can be maintained at par with that of the blank paper when 4% cationic starch is added along with the filler. These retention corroborate the findings of Lindstrom et al⁴. Since results of fillers decreases the internal strength of the sheet, the capability of cationic starch in maintaining internal bonding strength in presence of these fillers is a most important property.

It is believed that retention of fillers and pulp fines usually is most effective around the point of zero charge when the electrostatic repulsion forces cease to operate.

Adsorption of cationic starch reduces the originally present negative charge on the fines and fillers. Fig. 4 depicts the results of effect of addition of cationic starch on retention of fillers (clay).



The pulp in this case was beaten to 320 ml. CSF and had a consistency of about 0.8%. The pH of the system was 5.5. The filler added to the stock was about 20% clay based on the pulp weight. Sheets of 60 gm² were prepared on a laboratory sheet former and the retention of fillers on the pulp under these conditions was measured by determining the ash content of the sheets as usual. The ash contents of the sheets were plotted against the concentration of cationic starch on the pulp. It can be seen that ash content of the sheets increases with the increase of cationic starch on the pulp and reaches a maximum at about 2% of cationic starch after which the ash content of the sheets decreases. The maximum value of ash indicates the maximum retention of fillers which in turn indicates the maximum cationic demand of the pulp. Indirectly, this also should roughly indicate the zero mm zeta potential of the pulp. With higher concentration of cationic starch the charge on the fillers gets reversed which then stabilizes the dispersion and consequently lowers the retention of fillers.

CONCLUSION

1. The cationic starch prepared in the laboratory has been found to be an effective dry strength additive.

By incorporating the cationic starch, the strength of the paper can be considerably increased.

2. Using cationic starch alone (without using any anionic polymer into the system) paper with filler content as high as 40% can be prepared without any appreciable loss of dry tensile strength. Thus the opacity and brightness of the paper sheets can be improved.
3. The cationic starch prepared in the laboratory is also found to be effective as a retention aid.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks and gratitude to the Director, Regional Research Laboratory, Jorhat, for his kind permission to publish this paper.

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