Dry processed cationic starches and flours

Performance in kraft bag and filled bond paper

ABSTRACT
Quaternary cationic cereal starches and flours prepared by a semidry (15-18% moisture) process have been evaluated as wet-end additives in unbleached kraft bag and filled bond papers. A 32-in. pilot fourdrinier paper machine was used to compare the experimental products with commercial cationic potato and corn starches. The experimental products were equivalent or superior in performance to the commercial materials in respect to strengthening ability and filler retention capacity.

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The technical and economic feasibility of using semidry reaction conditions for preparation of cationic cereal products has been explored in prior studies (1). Corn and wheat flours were reacted in a semidry process with ethylenimene (3-4%, basis dry flour) to form cationic aminoethyl derivatives. Although the cost-performance ratio for the experimental materials was superior to the commercial cationic starches used in comparative studies (2), the hazardous properties of ethylenimene and its inclusion on a list of carcinogens (3), subsequent to the development of our experimental products, discouraged any commercial development of aminoethyl derivatives.

The economic and environmental advantages of a semidry reaction process have prompted additional studies to locate a more suitable, industrially acceptable, cationizing material. A quaternary salt, 3-chloro-2-hydroxypropyl trimethylammonium chloride, currently being marketed as a starch modifier in aqueous systems, has been adapted to a semidry reaction process (4). The resulting quaternary cationic starches and flours are stable, have a high degree of cationic efficiency, and have performed well in preliminary handsheet evaluations (5). Evaluations have, therefore, been extended to pilot-scale equipment to establish their comparative performance with commercial additives in an unbleached bag and a filled bond paper.

Conclusions
The "dry processed" quaternary cationic starches and flours provided strength increases and retentive capacity, in the paper products evaluated, that were commensurate with those normally achieved with commercial cationic starches of good quality. The experimental products are stable (no detectable change in performance after three years storage at room conditions), disperse easily, and present no unusual problems in handling or use.

The simplicity of the semidry reaction conditions not only minimizes processing costs but also alleviates pollution problems normally associated with aqueous preparation of cationic starches. Processing equipment and reaction conditions are such that the semidry process can be readily adapted to "on-site" preparation of the quaternary materials.

Results and discussion
Determining the potential of cationic materials as paper additives is difficult because of the interaction of its two primary functions—improving retention of fillers and fines and increasing strength properties. Other factors such as machine speed, furnish composition, other additives, point of addition, extent of white water recycling, broke reuse, etc. also affect performance of cationic products. Papermakers, therefore, tend to relate the credibility of performance data of wet-end, cationic materials to the scale of experimental trials.

We realize that the ultimate potential of a material can only be determined after extensive use under specific mill conditions. However, data obtained on our pilot papermaking facility have proven to be very reliable in projecting mill behavior and performance (2). Detailed analysis of pilot and mill data in the prior studies established the credibility of using comparative rather than absolute data in the pilot scale evaluations. The "dry processed" experimental starches and flours have, therefore, been compared directly with commercial cationic corn and potato starch whose performance is well established and documented in the literature for a wide range of applications. The commercial products, selected for their superior performance in the furnishes used in these studies, were used as "controls" for determining the relative performance characteristics of the experimental products and for projecting their behavior under mill conditions. Cationic efficiencies, an arbitrary measure of the amount of a standard anionic dye absorbed by a pulp-cationic starch complex of the experimental and commercial additives, as determined by a modified method of Mehltretter et al. (1, 6), were equivalent (98-100%).

A 32-in. pilot fourdrinier was used to prepare 73 g/m² filled bond and 100
g/m² kraft bag paper. Both commercial and experimental materials were dispersed with live steam injection, cooled to approximately 30°C, and then added, in line, at 0.5, 1.0, and 2.0% levels of addition. Stock pump addition was employed with the kraft bag paper, whereas both stock pump and headbox addition were used with the filled bond paper.

**Kraft bag paper**

Retention and dry strength increases obtained with the “dry processed” quaternary cationic flours and starches were typical of those obtained with quality commercial cationic starches (Table I). At the 1.0 and 2.0% levels of addition, no significant differences were observed in the performance characteristics of the three experimental and two commercial materials. Only at the lower level of addition (0.5%) was the anticipated difference in the two commercial materials. Only at the 2.0% level of addition were commercial “controls” (Table II) using a stock pump addition, the experimental products were comparable or superior to the commercial cationic corn starch and slightly inferior to the cationic potato starch. When added at the headbox, however, no significant differences could be detected between the experimental wheat starch and the cationic potato starch, and both were superior to the corn starch in filler retention. At the lower level of addition (0.5%), approximately 90% of the filler was retained in the fiber mat, and suspended solids were reduced by as much as 50%. With headbox addition, filler and fines retention decreased, as expected, with increasing amounts of cationic material.

**Reaction temperature**

The experimental products were prepared at both 25 and 60°C. Use of the higher temperature reduced reaction times from 3 days to approximately 6 hr. The end products were identical in cationic efficiency and performance. Although all products (25 and 60°C) were evaluated, only representative data for each material are presented in the tables.

**Efficiency of reaction**

Regardless of the reaction conditions used with the starches and flours (aqueous or semidry), reaction efficiencies of only approximately 50% can be achieved with the 3-chloro-2-hydroxypropyl trimethylammonium chloride. In the aqueous process, the majority of unreacted monomer (not reacted with starch) is removed during washing and recovering of the derivatized product. However, the unreacted monomer remains in the product prepared by the semidry process. Preliminary studies have shown that the excess monomer has no effect on performance of the cationic products in paper. Solvent extracted materials produced identical results in filled bond paper with that of the parent product (data not shown).

**Economics**

A detailed economic evaluation of the “dry processed” cationic starches and flours has not been undertaken. However, based on commercially projected selling costs of “dry processed” amine-ethyl flours (2), the quaternary products should be marketable at 20-22 cents/lb. This estimate is based on corn starch at 7.4 cents/lb and 3-chloro-2-hydroxypropyl trimethylammonium chloride at 90 cents/lb. The commercial cationic corn and potato starches used in these studies as “controls” were selling for 19 and 26 cents/lb, respectively, in carload lots.

**Experimental**

**Materials**

The experimental cationic starches and flours were prepared by the following process (4): 200 g (dry basis) of commercially obtainable starch or flour (moisture 10-14%) was placed in a laboratory sigma blade mixer. Calcium oxide (2.6 to 5.2 g) was added with mixing. Mixing was continued 30 min before addition (by spraying) of 28 to
86 g of a 50% solution of 3-chloro-2-hydroxypropyl trimethylammonium chloride in water. Mixing was then continued for approximately 5.5 hr. Samples reacted at 25°C were removed and stored for 3 days to allow the reaction to reach completion. For those reacted at 60°C, the reaction was complete after the initial mixing period. Final moisture of the samples varied from 15 to 18%. No additional treatment of the quaternary products was required prior to storage or use.

Commercial starches were selected from several that had been evaluated previously in similar types of furnish. The two used in these studies (a cationic cornstarch and a cationic potato starch) had cationic efficiencies of 99–100% and gave the highest overall strength benefits of those tested.

**Pilot paper machine**
A 32-in. (0.8 m) fourdrinier equipped with a 16-in. headbox (14-in. trim) was operated at 150 and 200 ft/min (0.8 to 1.0 m/sec) to prepare a 100 g/m² unbleached bag and a 75 g/m² filled bond paper, respectively. One hundred percent unbleached kraft refined to 480 ml CSF was used for the bag furnish (wire pH of 6.0). The bond furnish consisted of a 50:50 blend of hardwood-softwood kraft pulp refined to 480 ml CSF containing 1.0% resin, 2.0% alum, and 15% clay filler. The pH was controlled at 5.5 with sulfuric acid. The cationic flours and starches were added at 0.5, 1.0, and 2.0% levels of addition at either the stock pump or headbox manifolds using automatic proportioning equipment.

**Testing and analytical procedures**
Strength and surface properties of the paper were determined in accordance with TAPPI Standard and Provisional Methods. Starch and flour retention was estimated by a modified method (7) based upon TAPPI Suggested Method (T419 su-70) for determining starch in paper.

**Literature cited**
5. Unpublished results.


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