

Effect of Chlorine on the Starch Component of Soft Wheat Flour¹

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ABSTRACT

Changes that take place in the starch component during treatment of flour with chlorine were studied. Cake flour was treated with successive increments of chlorine (1.0 to 16.0 oz. per cwt.) and starch was then isolated from each sample of treated flour. The effect of the treatment was evaluated by the following indices: Pasting characteristics (Brabender Viscograph), swelling power, solubility, and water-binding capacity. The pasting characteristics of the parent flour were also tested. Baking tests of chlorinated flours (white layer-cakes) showed an optimum range within 1.0 to 4.0 oz. chlorine per cwt.; above these levels rapid deterioration of quality occurred. Starches isolated from flour treated with up to 4.0 oz. per cwt. gave hot and cold consistencies similar to those of the untreated flour; above this level chlorination caused drastic reductions of paste consistencies, which was attributed to the depolymerization of starch. Of the other starch properties studied, water-binding capacity increased consistently throughout the entire concentration range. Swelling power increased only slightly up to the 4.0 oz. per cwt. level, but then increased significantly at higher levels. Solubilities increased only above the 4.0-oz.-per-cwt. treatment level. Amylograms of chlorinated flour indicated a decrease of amylolytic power with increasing chlorination.

In the previous report (1), effects of chlorine treatment on the protein fraction of flour were described. The present paper, as another aspect of this study, reports changes induced by chlorine in the prime-starch component of flour. Evaluation was by physicochemical means, correlated with baking properties.

The chemical mechanism of the chlorine action on wheat starch was studied by Whistler and his group (2,3,4). They showed that chlorine causes depolymerization of starch polymers, the degree and type of which depend on the conditions of the reaction. At low pH, an emergence of aldehydic groups was observed; higher pH conditions yielded ketonic and carboxylic groups. These data, although suggestive of involvement of starch in chlorination of flours, were carried out at substantially higher levels of chlorine than are used in commercial practice and without an attempt to correlate these changes with the actual baking properties of flour.

Improvements of baking properties by chlorination were attributed by Alexander (5) to increased hydration capacities of treated starches. More recently, Sollars (6) fractionated soft wheat flours and, by interchanging fractions isolated from untreated and chlorinated flours in baking tests, demonstrated that chlorination improved both gluten and prime starch without producing significant changes in other flour components.

Youngquist et al. (7) suggested that the lipids associated with starch granules undergo chlorination, thereby improving the pasting properties of the starch component.

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MATERIALS AND METHODS

Flour and Chlorination

Flour and the treatment procedures were the same as reported in the previous study (1). Levels of 0, 1.0, 2.0, 4.0, 8.0, and 16.0 oz. of chlorine per cwt. of flour were tested.

Isolation of Starch

Prime starch was separated from untreated and treated flour by the dough procedure, exhaustively washed with distilled water, and air-dried in a flow of air at room temperature.

Viscosimetric Determination

The Brabender Viscograph was used for these measurements. The flour samples were pasted according to the conventional amylograph procedure (8), except that six parts of flour solids were used per 100 parts of buffer. An additional adjustment of pH to 5.35 with dilute sodium hydroxide solution was necessary with highly chlorinated flour. After the sample reached the pasting peak, the temperature was kept constant for 30 min., then cooled to 35°C. for an additional 30 min. This viscogram gave four important reference points: 1) peak, 2) consistency at 30 min. after peak as a measure of the hot-paste stability, 3) cold-paste consistency at 35°C., and 4) consistency after 30 min. at 35°C. as indication of the retrogradation rate of the paste. Starch viscograms were prepared in the same way as those with flours, except that pasting was conducted in distilled water, using nine parts of starch solids per 100 parts of water.

Other Measurements

Gelatinization ranges of starches were determined microscopically with a Kofler hot stage (9). Solubility and swelling powers were measured by the procedure of Leach et al. (10). Water-binding capacities of starches were determined by the method of Medcalf and Gilles (11).

Farinograms (constant flour-weight method), moistures, and pH values were obtained by conventional methods (8).

RESULTS AND DISCUSSION

Baking Results

According to previously reported baking tests (1) (white cake), levels of 1.0 to 4.0 oz. chlorine per cwt. flour were found beneficial to cake quality; the optimum level was 2.0 oz. per cwt.; above 4.0 oz. per cwt. a rapid deterioration was observed.

Viscograms of Flours

As a first approach in the detection of starch changes, viscograms of flours treated with 0, 1.0, 2.0, 4.0, 8.0, and 16.0 oz. chlorine per cwt. flour were prepared. The indices of these viscograms shown in Fig. 1 demonstrate a gradual increase of consistencies with each chlorine increment, reaching a maximum at 4.0 oz. chlorine per cwt., then decreasing rapidly with additional chlorine treatment. The initial rise in paste consistencies with increasing treatment levels is most likely owing to a gradual inactivation of α -amylase.

An interesting relationship was obtained when the flour pH values of treated flours were plotted against consistency indices of the pastes (Fig. 2). Considering the pH range above 4.0, it is evident that the paste consistency was at its minimum within the range for optimum α -amylase activity and that it increased with the decreasing pH owing to the acid sensitivity of the enzyme (12). This indicates that substantial inactivation of the enzyme may occur in a semi-dry state if the pH of flour is lowered sufficiently. Below pH 4.0, chlorination caused rapid reduction of paste consistencies, which was attributable to the depolymerization of starch by chlorination.

This view is supported by the effect of silver nitrate on the pasting characteristics of this flour. When α -amylase was inactivated by treating flour with 0.25 μ mole of silver nitrate per gram, the hot peak viscosity reached 960 B.U. Since this was higher than the maximum recorded with treated flour, a partial inactivation of α -amylase by chlorination was indicated.

The viscogram of flour treated with silver nitrate (Fig. 3, left) demonstrated insignificant changes in hot- and cold-paste consistencies, indicating no substantial changes in the starch within the range of 0 to 4.0 oz. chlorine per cwt. flour. A closer look at the viscograms (Fig. 3, right) revealed, however, that chlorine treatment produced a faster rise in flour viscosities only within the temperature range of about 50° to 75°C. This more rapid increase in viscosity with the degree of chlorination is noteworthy since it may be of major importance in baking cake batters by permitting an optimum retention of the leavening gas and increasing the stability of batters during the early oven stages. Above this range of treatment, drastic changes both in starch and in proteins (1) occurred, which were reflected in a rapid deterioration of the baking properties of the flour.

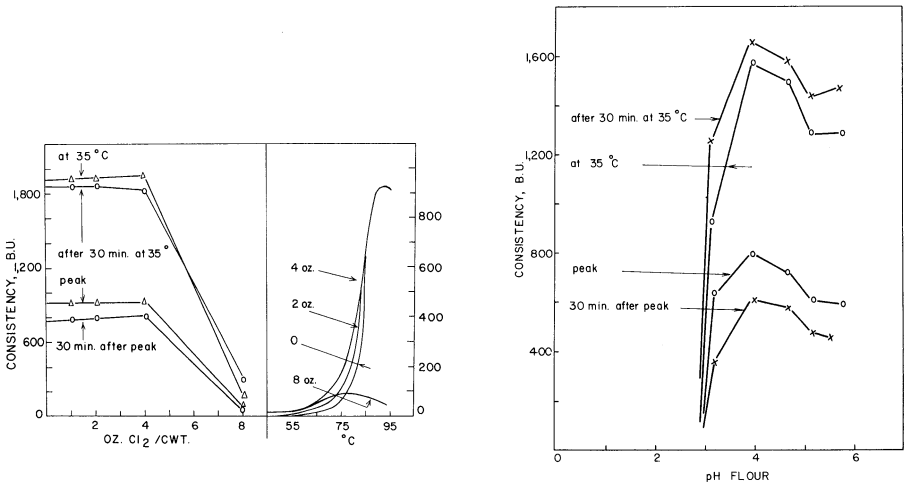


Fig. 1 (left). Left frame: Effect of chlorination on viscogram indices of flour; right frame: effect of chlorination on pasting curves of flour.

Fig. 2 (right). pH values vs. consistency indices of flour.

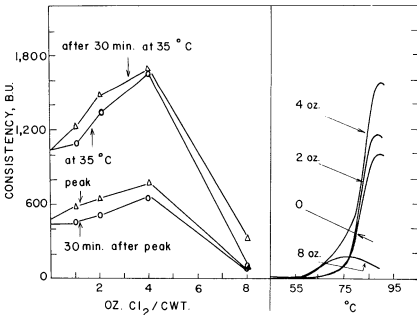


Fig. 3 (left). Left frame: Effect of chlorination on viscogram indices of enzyme-inactivated flour; right frame: effect of chlorination on pasting curves of enzyme-inactivated flour.

Fig. 4 (right). Left frame: Effect of chlorination on viscogram indices of starch from treated flour; right frame: effect of chlorination on pasting curves of starch from treated flour.

Viscographic Characteristics of Starches

Changes in the starch component may not be properly assessed from the flour viscograms because of possible interference of other flour components. Therefore, starches isolated from these flours were further studied. Their viscographic properties in Fig. 4 indicate little changes in paste consistencies up to the level of 4.0 oz. chlorine per cwt. of flour. Above this level, a rapid degradation of starch was evident. This trend of the action of chlorine is in a general agreement with the viscographic data obtained with α -amylase-inactivated flour (Fig. 3). There was, however, a significant difference in the initial rise of consistency between the starch and flour which is evident from inspection of viscograms shown in Fig. 3 (right) and Fig. 4 (right). Whereas the rate of increase was greater in flour with increasing chlorine levels (up to the level of 4.0 oz. per cwt.), no such effect was observed with the starches isolated from the respective flours. Their viscograph curves were practically identical and comparable to the starch from the untreated control flour.

The difference between the pasting behavior of flour and starch indicated that the thermal setting rate of the flour system is not due to a change in the mechanical properties of the starch paste. Modification of starch was not demonstrated in the simple starch-water system. Simultaneously with the present results, Youngquist et al. (7), reporting a viscographic study of cake batters, showed similar effects. Chlorination accelerated the setting of cake batters, but was without an apparent effect on the pasting rate of the isolated starches. They postulated that the flour system contains a factor which is responsible for the changed characteristics of the starch component and which is lost during the separation of starch from flour. Further, they presented circumstantial evidence that the lipids associated with the starch granules undergo chlorination and are responsible for this effect. Based on Sollars' (6) observations that both gluten and starch are primarily involved in the improving action of chlorine, it appears to us that the change of pasting characteristics caused by chlorination may be explained by interactions of starch and gluten; it is also possible that other components of the batter systems may also take part or may accentuate these interactions.

TABLE I. GELATINIZATION TEMPERATURES OF CHLORINATED STARCHES

Chlorine, oz./cwt. flour	Gelatinization, °C.		
	Initiation	Mid-point	Final
0	54.0	58.0	61.5
2	55.0	58.5	61.5
4	55.0	58.0	61.0
8	55.0	58.0	61.5
16	58.0	61.0	65.0

Gelatinization Ranges

Starch granules at all levels of treatment retained birefringence and their gelatinization ranges were not materially altered (Table I). Apparently the chlorine did not affect the crystalline regions of the starch granules but was confined essentially to the surface and amorphous areas. At higher levels of treatment starch granules became difficult to disperse, forming clusters and showing high sedimentation rates which indicated surface damage to the starch granules. Although the morphological integrity of the granules was preserved within the gelatinization ranges, the swollen granules derived from heavily treated flour were fragile and at higher temperatures tended to lose integrity, a condition which was supported by viscographic and solubility data.

Solubilities and Swelling Powers

These data are shown in Figs. 5 and 6. The swelling powers of starches within the 1.0 to 4.0 oz. chlorine per cwt. treatment range increased slightly above the control for the temperature range 60° to 80°C.; above 80°C. no appreciable differences in swelling were observed. Treatment above these levels induced increased swelling. Solubilities followed a pattern similar to the swelling powers

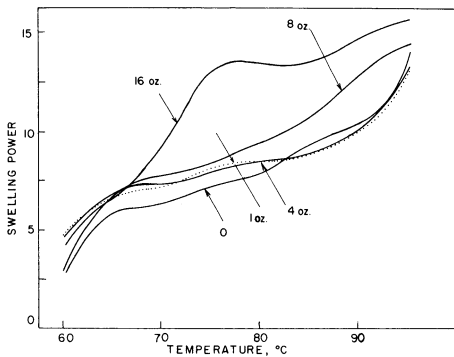


Fig. 5 (left). Swelling powers of starches from flour with varied chlorine treatments.

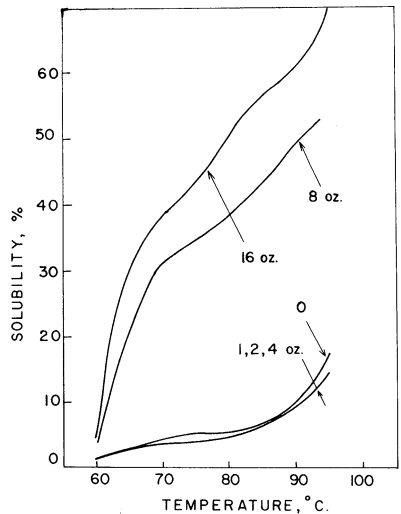


Fig. 6 (right). Solubilities of starches from flour with varied chlorine treatments.

(Fig. 6). Practically no changes in solubility were observed until the level of 4.0 oz. chlorine per cwt. was passed, then a high increase was recorded.

Water-Binding Capacity

As is evident from Table II, the water-binding capacities of the starch and of the parent flour increased throughout the entire range of treatment. In view of the swelling, solubility, and viscographic patterns, this increase of the hydration properties of starches with lower levels of chlorination was due mainly to increased intergranular binding of water rather than to higher sorption of granules. Only at higher levels (above 4.0 oz. per cwt.) did increased swelling power indicate a relaxation of intragranular associative bonds, resulting in higher sorption capacities of the granules. Farinograph absorptions given in the same table show a similar trend to the water-binding capacities of starches.

CONCLUSIONS

The present evidence indicates that chlorination of flour produces changes in the characteristics of the starch component. Within the useful range of chlorination, few changes were observed which might have some bearing on the cake-baking properties of flours. Baking tests reported previously (1) showed 4.0 oz. per cwt. to be maximum usable level. Since the same flour was used in the present experiments, these data are directly applicable to the present discussion. Within this range, no change in pasting characteristics were indicated by starch viscograms; neither were there appreciable differences in swelling power, solubility, or gelatinization ranges. Chlorination gradually and partially inactivated α -amylase, a change which is probably of minor importance in preparation of cakes since the formation of the cake structure takes place at pH conditions that are rather adverse for amylolysis. On the other hand, the hydration capacities were consistently increased with each chlorine increment. The effect of chlorination on the flour viscograms was noteworthy; the rate of the initial rise of the paste consistency of flours increased with chlorination. Since no such effect was observed with starches isolated from chlorinated flour, it appears that it was caused by interaction of starch with other components of flour. Possibly the surface of the granules was "activated" by the action of chlorine, which facilitated formation of starch-lipid or starch-protein complexes, resulting in stabilization of the cake batter during baking. This type of change, evidenced by the pasting characteristics of flour and hydration capacities of the isolated starch, should be considered in further studies of cake-batter systems.

TABLE II. EFFECT OF CHLORINATION ON WATER-HYDRATION CAPACITY OF FLOUR AND STARCH

Chlorine, oz./cwt. flour	Farinogram Flour Absorption (14% m.b.) %	Water-Binding Capacity (starch) %
0	50.1	73.91
1	51.9	77.41
2	52.4	82.23
4	53.9	83.37
8	53.6	83.50
16	56.1	89.10

Acknowledgment

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