Effects of Chlorine on Flour Proteins, Dough Properties, and Cake Quality[1]

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ABSTRACT

Chlorine was applied to cake flour at levels of from 0 to 16 oz. per cwt. The treatment reduced the pH, bleached the flour pigments over the entire range, and improved the cake-baking properties of flour up to 4.0 oz. per cwt. Above this level the effect on pH and pigments was sharply reduced and the volume and quality of cakes deteriorated rapidly. Farinograms indicated that the stability of doughs was first increased by chlorine treatment of flour (up to 2.0 oz. per cwt.), but then was rapidly reduced by higher treatment levels. Each increment of chlorine produced an increase in the water absorption of farinograph doughs. The flour proteins were progressively cleaved by each increment of chlorine as evidenced by the increasing extractability of proteins in water and acetic acid. This change was attributed to the dispersing, hydrolytic, and oxidative actions of chlorine. The oxidative effect of chlorine was further reflected in the change of SH content and in the oxidative degradation of aromatic amino acids. Chlorination of tyrosine was also detected. The significance of these reactions for the quality of cake flours is discussed.

It is a common practice to improve the cake-baking properties of soft wheat flours by chlorination. Cakes made from flours treated with optimum amounts of chlorine are higher in volume and have finer grain and texture than those prepared from untreated flours. Chlorine treatment also increases the ability of flour to carry higher levels of sugar and shortening, permitting the use of "high ratio" formulas desired by bakers because of improved eating quality of the products.

The mechanism of the chlorine action on flour has been the subject of a number of investigations. Sollars (1,2) demonstrated by means of cake flour fractionation

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and reconstitution that chlorine bleaching improves the baking properties of the gluten and prime starch components but reported that the effect on other flour fractions was too small to be important. Depolymerization of pentosans due to chlorine treatment was observed by Whistler and Pyler (3). Changes in lipids were detected by Daniels (4) who showed that the linoleic acid content of flour was lowered by chlorination. Recently, Youngquist et al. (5) attributed the improving effect to the formation of chlorine derivatives of fatty acids within the starch granules. These reports serve to indicate that chlorine has a multiple effect on flour, involving many classes of constituents.

The present study was initiated to examine systematically the chemical action of chlorine on protein, starch, pH, and carotene content of flour; on the rheological properties of doughs; and on cake-baking performance. Results of this investigation, except for those related to the starch component which are reported separately (6), are given and discussed in this paper.

Some part of the present work repeated earlier investigations, such as those by Bailey and Johnson in 1924 (7) on the effect of chlorine on the pH of flour; by Bohn in 1934 (8) on the improving effect of chlorine on cake volume and score; and by Alexander in 1933 (9) on the bleaching effect of chlorine. In these studies moderate levels of chlorine (1 to 2 oz. per cwt.) were used, bringing down the pH of flour-water suspensions to about 4.4. However, in order to fully explore various effects of chlorine on flour constituents, dough properties, and cake quality, a wide treatment range of chlorine was employed in the present study. The repetition of earlier investigations was necessary to present completely comparable data.

MATERIALS AND METHODS

Flour

Cake flour commercially milled from soft red wheat grown in eastern and central Ohio was used throughout this study. Its protein (N X 5.7) and ash contents were 8.7 and 0.31%, respectively (14% m.b.).

Methods

Chlorine treatments of 1 to 16 oz. per cwt. were done in a Wallace & Tiernan laboratory bleacher using liquid displacement of chlorine gas to control the treatment level. Carotene content and pH were measured and farinograph tests conducted according to AACC procedures (10). Protein extractability was performed as described previously (11). The SH content was determined according to the method of Sokol et al. (12), as modified by Tsen and Hlynka (13). Ultraviolet spectra of water and acetic acid extracts of flour were prepared with a Beckman DU spectrophotometer.

Baking Tests

White layer cakes were baked using 100.0% flour, 96.1% sugar, 1.5% salt, 5.75% baking powder, 11.5% nonfat dry milk, 5.75% dried egg albumin, 39.0% shortening, and 104% water. A multi-stage mixing procedure was used.

RESULTS AND DISCUSSION

pH of the Water Suspension of Flour Treated with Chlorine

Table I shows the pH values of water-flour suspensions. As expected, the pH

TABLE I. pH OF THE WATER SUSPENSION OF FLOUR TREATED WITH CHLORINE

Chlorine Treatment Level oz./cwt. flour	pH of Suspension
0.0	5.68
1.0	4.89
2.0	4.51
4.0	3.63
8.0	2.69
16.0	2.06

decreased with increasing levels of chlorine. A rapid, almost linear decrease in pH was found from 1.0 to 4.0 oz. of chlorine per cwt. but at higher levels the decrease was minor.

Bleaching Effect

Figure 1 shows the bleaching effect of chlorine as indicated by the pigment content. The results, as demonstrated by a number of workers, show clearly that chlorine can effectively bleach the carotene-type pigments of flour. The amount of chlorine required for bleaching was about 2.0 oz. per cwt. under the present conditions. Beyond this level, additional amounts of chlorine did not effectively reduce the carotene content to any further extent.

Changes in Dough Properties

Figure 2 presents farinograms of flour treated with chlorine. It can be seen from this figure that an increase in stability with chlorine treatment levels up to 2.0 oz. per cwt. is followed by a rapid decrease with higher chlorine levels. These changes in dough properties, an initial strengthening followed by rapid weakening, reflect the oxidative and hydrolytic actions of chlorine on the flour proteins. At the same time, the chlorine treatment increased the water absorption of the flour. This change can be attributed to increased hydration capacities of starch granules (6). Pentosans which are depolymerized (3) under these conditions would be expected to lower the absorptive capacity of flour.

Baking Test Results

Baking results of flours treated with various levels of chlorine are presented in Table II and Figs. 3 and 4. As evident from Table II and Fig. 3, chlorine treatment,

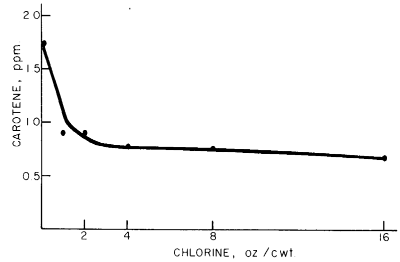


Fig. 1. The bleaching action of chlorine.

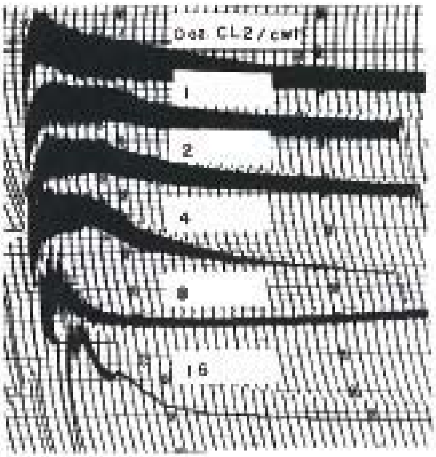


Fig. 2. Farinograms of mixing the treated flour with water. The absorption shows a corresponding increase, 51.9, 52.4, 53.9, 54.6, and 56.1% with increasing treatment levels of chlorine of 0, 1, 2, 4, 8, and 16 oz. per cwt.

Fig. 3. Cakes made from flour treated with various levels of chlorine.

within the range of 1.0 to 4.0 oz. per cwt., definitely improved the external appearance and increased cake volume. However, the treatment levels of 8.0 to 16.0 oz. per cwt. resulted in a large drop in volume and whitening of the crust color. Similar effects of over-chlorination were reported by Kissell (14). Figure 4 shows the internal appearance of cakes. The grain, texture, and color of the cakes all were improved with chlorine treatment up to 4.0 oz. per cwt., and the best cake resulted from flour treated with 2.0 oz. per cwt. Levels of treatment above 4.0 oz. per cwt. destroyed normal grain, texture, and symmetry of cakes.

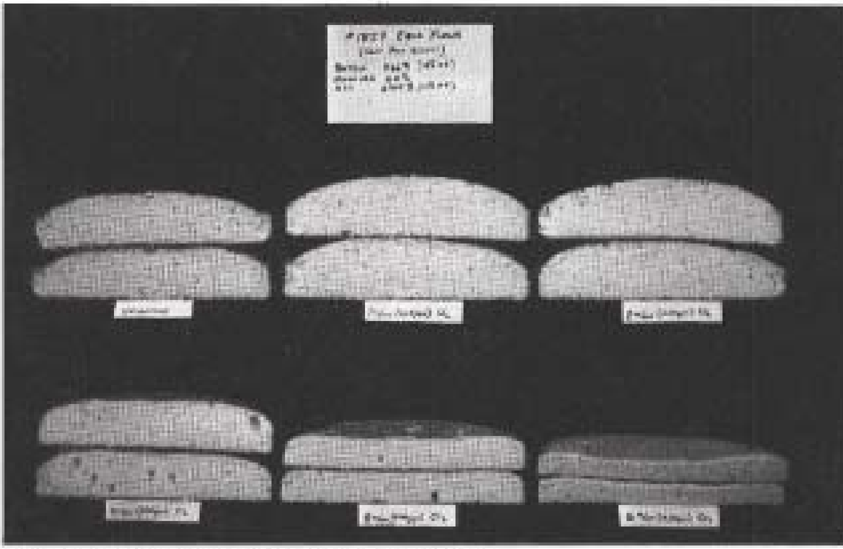


Fig. 4. Cross-view of cakes made from the treated flour.

TABLE II. BAKING RESULTS OF FLOUR TREATED WITH CHLORINE

Treatment Level oz./cwt.	p.p.m.	Volume cc.	Crust[a] (15)	Symmetry (5)	Silkiness (5)	Tenderness (10)	Grain (35)	Color (30)	Total Score
0	0	1,050	10	2	3	7	28	20	70
1	625	1,200	13	3	4	8	30	26	84
2	1,250	1,200	14	4	5	10	34	28	95
4	2,500	1,125	14	4	4	7	32	29	90
8	5,000	700	8	2	2	2	20	25	59
16	10,000	575	0	0	0	0	0	15	15

[a]Numbers under each quality index indicate maximum value.

Effect of Chlorine on Flour Proteins

Changes in the protein fraction of flour by chlorination were followed by measuring the effects on a) solubility, b) aromatic amino acids, and c) SH groups.

(a)*Solubility Changes.* Table III shows that the amount of protein extractable by 0.05N acetic acid decreased slightly with increasing levels of chlorine. On the other hand, the amount of water-extractable protein showed a marked increase with chlorine treatment. This increase in water-soluble protein was caused in part by the lowering of pH. However, when the pH of the flour-water suspension was adjusted to pH 5.15 for extraction, a substantial increase in extractability was still found with the chlorine-treated flour, except for that treated with 16 oz. per cwt. It seems probable that at the 16.0 oz. level, proteins were altered to such an extent that they remained insoluble even when the pH was brought to 5.15. In addition, it is known that protein solubility is influenced by ionic concentration. The flour at pH 2.06 (16 oz. chlorine) would, when neutralized, contain a relatively high ionic

TABLE III. EXTRACTABILITY OF NITROGEN IN THE CHLORINE FLOURS BY ACETIC ACID AND WATER

Treated oz.Cl_2/cwt.	0.05N Acetic Acid mg.N/g. sample	Water No pH Adjust mg.N/g. sample	pH 5.15 mg.N/g. sample
0	14.07	7.61	7.61
1	13.97	10.03	9.01
4	13.69	12.93	9.19
16	13.29	12.55	4.18

concentration which may also depress the solubility of protein in the flour tested with 16 oz. chlorine per cwt. Nevertheless, at moderate chlorine treatment levels, the increase in water-extractable protein suggests that chlorine cleaves high-molecular-weight proteins into smaller, water-soluble fragments by its dispersing, hydrolytic, and oxidative actions.

(b) *Reactions with Flour Proteins.* The oxidative action of chlorine on water- and acetic acid-soluble proteins was detected by changes in the UV spectra of the extracts. The greatest changes in absorbance occurred in a UV range of 250 to 399 nm. Therefore, spectral curves were made in that range for extracts from the flour treated with different levels of chlorine. As presented in Fig. 5, the absorbance at 280 nm. at first increased with chlorine treatment, showing a maximum height at the 1 oz. per cwt. level. Further treatment showed a decrease in absorbance. The water extract of flour treated with 16 oz. chlorine per cwt. did not show an absorbance peak at 280 nm., which indicated that aromatic groups of amino acids such as tyrosine, tryptophan, and phenylalanine had been greatly modified by chlorine.

It was not clear why the absorbance increased in extracts from flour treated with chlorine. Since all the extracts were adjusted to the same nitrogen content (0.13 mg. per ml.) for the absorbance measurements, the increase was apparently not due to the change in protein content of the extracts. In an attempt to find some clue to this, tyrosine, tryptophan, and phenylalanine solutions were treated with various amounts of chlorine, as indicated in Table IV. Results show that the absorbance at 280 nm. increased with chlorine treatment for tyrosine but not for tryptophan or

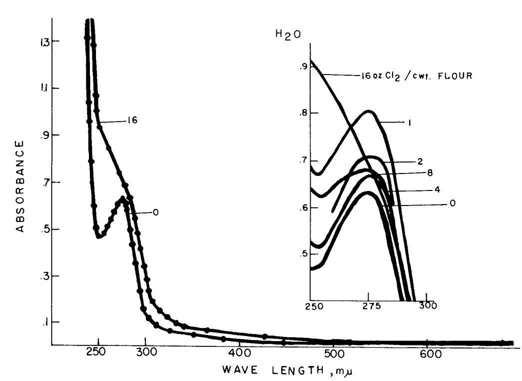


Fig. 5. Spectrum curves of water extracts from the treated flour.

TABLE IV. CHANGES IN ABSORBANCE OF TYROSINE SOLUTIONS ($2.5\ 10^{-3}$ M) TREATED WITH CHLORINE

Chlorine Treatment Level ml./10 ml. solution	Absorbance at 280 nm. (1:50 dilution)
0.5	0.328
1.0	0.359
2.0	0.430
3.0	0.445

phenylalanine. Thus it appears that an electrophilic substitution of hydrogen by chlorine might take place in the tyrosine group which causes an increase in absorbance. In addition, preliminary work on the amino acid analysis of flour and chlorine-treated flours showed the loss of tyrosine in the treated flour. However, additional studies are required to examine further the action of chlorine on the aromatic amino acids in flour in relation to the change in absorbance at 280 nm. of the extracts.

The spectra of acetic acid extracts of flour proteins are presented in Fig. 6. The changes observed were analogous to those found in the water extracts.

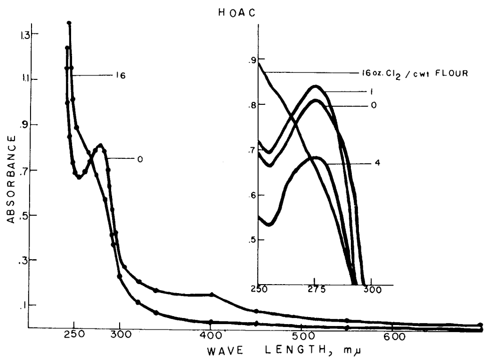
All these findings suggest the possible occurrence of chlorination of tyrosine in flour proteins even at the normal or practical chlorine treatment levels of 1 to 2.0 oz. per cwt.

(c) *Oxidation of Sulfhydryl Groups*. An additional study was made to ascertain whether chlorine oxidized SH groups in flour, as do other flour improvers. Results, given in Fig. 7, show that chlorine can oxidize SH groups in flour, which explains its maturing effect in flour doughs. However, the oxidative action of chlorine was not as great as observed for other improvers commonly used in the milling and baking industry for maturing.

CONCLUSIONS

Reaction of chlorine with flour produces three distinct changes: bleaching of flour pigments, reduction of pH, and chemical modification of flour components.

The degree of treatment is critical for its effect on flour. Under present



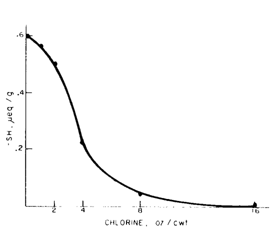


Fig. 6 (left). Spectrum curves of acetic acid extracts from the treated flour.

Fig. 7 (right). Oxidation of sulfhydryl groups by chlorine in flour.

experimental conditions, the optimum level of treatment was found to be 2 oz. per cwt.; up to 4.0 oz. per cwt., a cake superior to that from the untreated flour was produced. Beyond this level, additional chlorination was less effective in producing further bleaching and lowering of the pH. Moreover, the baking properties deteriorated drastically. It appears that important chemical changes in several of the flour components are produced by chlorination which, although beneficial at low levels of modification, are deleterious in over-chlorinated flours. So far as the commercial practice is concerned, the treatment level of chlorine generally varies from 0.5 to 2.6 oz. per cwt. of flour.

The inter- and intramolecular hydrogen bonds of the protein molecules are gradually broken by the action of chlorine, which causes an increased dispersibility of proteins. Concurrent with these changes, chlorine cleaves peptide bonds and lowers the pH of the flour. All these reactions tend to solubilize the gluten proteins.

Another type of reaction involving proteins can be attributed to the oxidative power of chlorine. This produces some degradation of the aromatic amino acids and oxidation of SH groups. A substitution with chlorine on the aromatic ring of tyrosine was suggested by the spectroscopic data.

All these reactions proceed simultaneously throughout the entire range and it is therefore possible that at least some of them contribute to the improving effects of chlorine. One may speculate that in cake batters the proteins solubilized by the action of chlorine may be more suitable than the insoluble proteins for building the proper cake structure. The solubilized proteins may also act more effectively as complex-forming agents, and thus permit a better incorporation of the shortening. The chloro-derivatives of tyrosine and possibly of other aromatic amino acids may interact with other flour and/or batter components, contributing to the structural stability of cakes. Oxidation of the SH groups indicates that chlorine performs a maturing action in flour, but this reaction is unlikely to be important since the gluten strength is not a critical factor in cakes.

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