

# Functionality in White Layer Cake of Lipids From Untreated and Chlorinated Patent Flours. I. Effects of Free Lipids<sup>1</sup>

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## ABSTRACT

Commercial unchlorinated soft red winter patent flour (pH 5.8) was treated to pH 5.2 (low), pH 4.8 (intermediate), and pH 4.0 (high) levels using 560, 1,120, and 2,240 ppm of chlorine gas, respectively. Hexane-extractable (free) lipids were removed by exhaustive refluxing with the solvent. Baking performances of the hexane-extracted (defatted) flours were poor and about equal, regardless of chlorine treatment. When lipids were returned to the respective extracted flours, the original baking quality of the chlorinated flours was restored. Cake volume increased with increasing chlorination to a maximum at pH 4.8, then decreased at pH 4.0. When lipids from pH 4.0 (highly chlorinated)

flour were added to the defatted flours of low and intermediate chlorine treatment, baking performance was inferior to the responses with their own lipid extracts. Addition of lipids from untreated, low, and intermediate chlorination rate sources improved baking function of the highly chlorinated flour residue. In a parallel test in which the same chlorine treatments were applied to hexane-extracted unchlorinated flour, a similar set of responses was obtained, but the combination of variables yielding acceptable performance was restricted to low and intermediate chlorine rates. The importance of the presence of free lipids *in situ* at the time of chlorination was confirmed.

Cole et al (1960) and Kissell et al (1971) have demonstrated the importance and functionality of the free-lipid fraction from soft wheat flour in the sugar-snap cookie (Finney et al 1950). Yamazaki and Donelson (1976) have shown the critical importance of the absence of lipids at the time of aqueous fractionation of flour to achieve a successful cookie from reconstituted dry blends. Seguchi and Matsuki (1977) reported the functional importance of flour lipids, particularly the polar components that can be extracted with water-saturated butanol, to the volume and structure of a basic Japanese pan cake.

The practice of enhancing the baking performance of flours by chlorination complicates study of the contributions of flour fractions to function in cake-batter systems. We undertook to determine the functional contribution of chlorination *per se*, and of chlorine concentration in particular, to both the free-lipid fraction and extracted flour residue when baked in white layer cake batters (AACC 1976). The importance to baking performance of the presence or absence of free lipids at the time of chlorination also was determined.

This work is the basis for a continuing study of the functionality of nonpolar and polar lipid fractions, individual lipid components, and the lipid interaction with level of shortening emulsification and of the relation of lipids to the other four traditional flour fractions.

## MATERIALS AND METHODS

Soft red winter patent flour was obtained in unchlorinated (pH 5.8) condition from an Ohio mill. Analytic data for the flour were ash, 0.40%; protein ( $N \times 5.7$ ), 9.64%; and hexane-extractable (free) lipids, 0.92% (all on dry weight basis).

The untreated patent was chlorinated in 1.5-kg portions in the

Wooster reactor (Kissell and Marshall 1972) at levels defined in terms of the quantity of gas required to give a nominal treatment for cake baking purposes, reducing the flour pH from 5.8 to 4.8, i.e., the 1.0 $\times$  treatment. The actual chlorine treatments were 0.5 $\times$ , 560 ppm; 1.0 $\times$ , 1,120 ppm; and 2.0 $\times$ , 2,240 ppm, representing low, intermediate, and high rates, respectively. Three flour lots were chlorinated at each dosage; lots were combined and blended by treatment.

Three kilograms of each flour was loaded in small (350-g) cloth bags and extracted exhaustively by refluxing with hexane in a large Soxhlet-type apparatus (Clements 1977). Extracts were concentrated, filtered, and diluted with hexane so that 1.0 ml of solution contained lipids from 2.25 g of flour. Lipid yields were determined gravimetrically from aliquots by evaporation and drying for 1 hr at 100°C.

We recognize that certain more polar lipids are not removed from flour by hexane extraction. Our baking results show that such lipids, although present in our extracted flours, are ineffectual in promoting cake performance. Residual polar lipids therefore were not considered to be functional components in this experiment and were not determined. In the present context, hexane-extractable lipids are defined as free lipids, and hexane-extracted flour residues are considered to be defatted.

Lipids were returned to hexane-extracted flours by contact wetting (Kissell et al 1971) with the requisite volume of solution. Hexane was removed from the reconstituted mixtures by stirring intermittently during 2 hr of aeration in a fume hood.

For thin-layer chromatography (TLC), the extracts were streaked onto precoated silicic acid plates at the rate of 500  $\mu$ g of lipid/cm. Chromatograms were developed in nonpolar solvent A (hexane/diethyl ether/acetic acid, 70:40:3), polar solvent C (chloroform/methanol/water, 65:25:4), or intermediate-polarity solvent B (1:1 mixture of solvent A and solvent C). For lipid detection, the plates were dipped in a solution of 3% cupric acetate in 8% phosphoric acid and heated for 30 min at 130°C (Clements 1977).

In a second test series, hexane-extracted control flour was chlorinated at the same rates of dosage given above. Moisture content of the extracted flour was adjusted to 13% before chlorination.

Baking tests were conducted with defatted flours and flours to which lipids were returned (reconstituted). The defatted control flour, the serially chlorinated and then defatted flours, and the defatted and then chlorinated flours were reconstituted in all possible combinations with lipids extracted from the control and

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serially chlorinated flours, which were all baked in triplicate.

The white layer cake method (AACC 1976) was used throughout. The published formula weights were reduced to 55% so that the batter per mix was enough for one 8-in. layer (425 g). Batters were prepared to contain 6.0% baking powder and 160% water (flour weight basis); the absorption level was found to be optimum with the 1.0× (intermediate) chlorination treatment. Layer volumes were measured by the bulk density of displaced rapeseed method. Internal appearance scores were judged as the consensus of two operators (LTK, JRD) using a modification of the AACC Method 10-90 scoring system. Components of score were cell distribution, 10 points; cell size, 10 points; cell-wall thickness, 10 points; overall grain appearance, 16 points; and color, 10 points. Score sums were adjusted to a total of 100 possible points.

No other modifications were made, but we emphasize that we have found this method to be sensitive to the emulsification properties of shortening. Our tests were conducted with a specific lot of commercial high-ratio shortening (Sweetex, Procter & Gamble Co., Cincinnati, OH); the use of other shortening samples with different emulsification ability was found to give altered results. A discussion of lipid/shortening/emulsifier interactions is

beyond the scope of this article, but we believe that such interactions may account for some of the disparity among results of workers in this field.

## RESULTS AND DISCUSSION

The pH responses to chlorination of the flours before and after lipid extraction are given in Table I, as are the average yields of free lipids for each chlorine treatment of whole flour. The pH values were 0.1–0.2 units lower for whole flours than for their defatted counterparts. The difference indicates that less chlorine was required per unit pH change for whole patent flour than for its defatted residue. The mean yield of free lipids increased slightly with increasing chlorine dosage.

Figure 1 shows TLC patterns of free-lipid extracts from the untreated and chlorinated flours. The most apparent effect of increasing chlorination was the development of severe "tailing" between the component bands. As chlorine rate increased, the intensities of several bands, which correspond primarily to lipids of low and intermediate polarities, decreased, whereas the intensities of a few bands, which correspond to diglycerides, increased. Generally, however, the 0.5× lipids were similar to the control lipids, and only the 2.0× lipids were markedly different from the control.

Basic baking responses of this chlorination series are shown in Fig. 2. The control (whole flour) column of cakes shows that both the 0.5× flour (pH 5.2) and the 2.0× flour (pH 4.0) performed substantially better than did the untreated flour in volume, contour, and internal appearance score. Optimum results for this series were obtained with the 1.0× flour (pH 4.8). These responses agree with expected behavior. Least significant difference at the 10% level of confidence for the overall range of treatments was  $\pm 37$  cc for volume and  $\pm 8.6$  for score.

Figure 2 shows that all the defatted flours performed about equally with respect to cake volume, but grain scores were higher than for the untreated control flour. When its own free lipids were returned, each flour produced a cake that resembled respective control in volume, contour, and score. Usually, we find the return of lipids to defatted flour by contact wetting results in larger volume and higher grain scores than in the cake from the original flour. The enhancing effects on cake quality may be due to the relocation of functional lipids to the surface of flour particles, where they are more readily available to act as functional hydrophilic emulsifiers during batter preparation.

To ascertain the effects of chlorine treatment level on the extracted lipids and defatted-base flours, we baked cakes with 16 reconstituted flours, which represented all possible combinations of the four flour bases and four lipid extracts. Each base received an

TABLE I  
Chlorine Treatments, pH Values, and Yields  
of Free Lipids From Commercial Cake Patent

Chlorine	Treatment (ml/g)	Rate (ppm)	Flour pH		Free-Lipid Yield <sup>a</sup> (%)
			Whole	Defatted	
0	0	0	5.78	5.76	0.92
0.5×	0.19	560	5.23	5.32	0.90
1.0×	0.38	1,120	4.80	4.96	0.93
2.0×	0.76	2,240	4.02	4.23	0.97

<sup>a</sup>Dry weight basis.

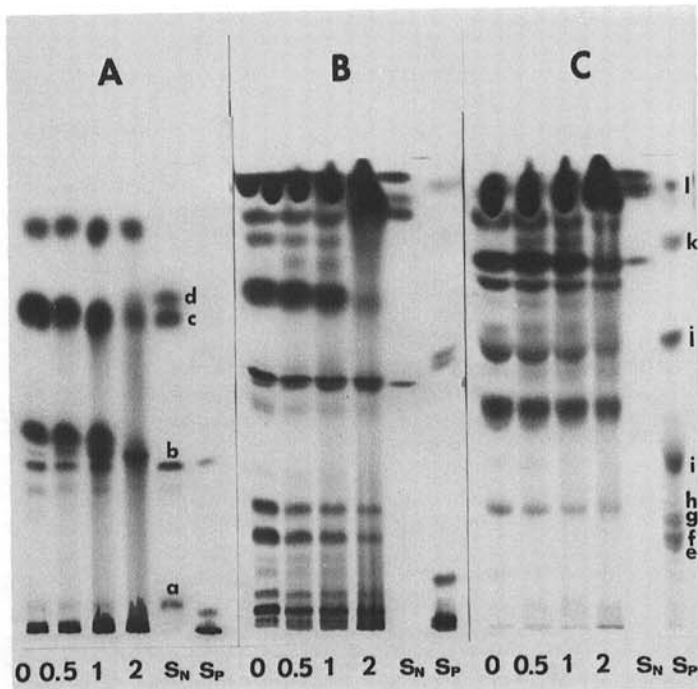


Fig. 1. Thin-layer chromatograms of free-lipid extracts from patent flour without chlorination (0) and with low (0.5), normal (1), and high (2) levels of chlorination. Nonpolar reference standards ( $S_n$ ) are monoglycerides (a), diglycerides (b), triglycerides (c), and fatty acid methyl ester (d). Polar references ( $S_p$ ) are sphingomyelin (e), phosphatidylserine (f), phosphatidylethanolamine (g), phosphatidylcholine (h), sulfatide (i), cerebroside (j), and ceramide (k). Development was by solvents that were nonpolar (A), intermediate in polarity (B), and polar (C). See text for compositions.

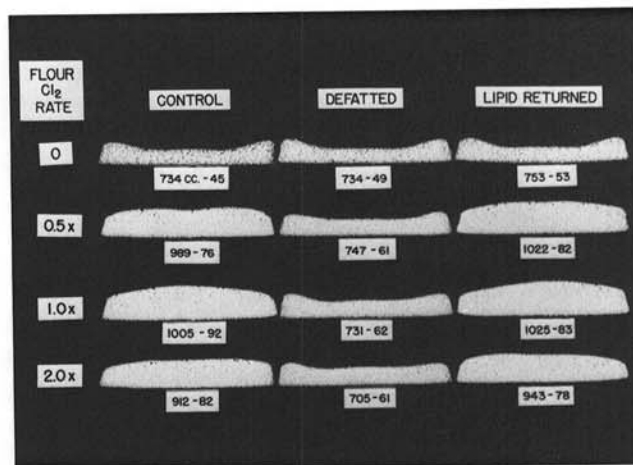


Fig. 2. Cross sections of cakes made from serially chlorinated patent flours: control (whole), defatted, and with lipids returned (reconstituted by contact wetting). Boxed numbers give cake volume and internal crumb score (100-point scale).

amount of lipid determined by the yield of the specific lipid applied (Table I). Figure 3 shows half cross sections of the resulting cakes. When lipid extract from unchlorinated flour was applied to the defatted residues, increases in the chlorine-treatment level of the base resulted in increased volume and score. Although the 1.0 $\times$ -base cake was unacceptable in terms of the desired volume of 975 cc or greater and score of 80 or above, it was significantly better than the completely unchlorinated product. At the high chlorine rate, application of untreated lipids gave a volume of about 1,000 cc, but cell structure was somewhat coarse. All batters containing unchlorinated lipids were smooth, glossy, yellow, and slightly thin in apparent viscosity.

In Fig. 3, the column of cakes containing 0.5 $\times$  lipids shows improvement with increasing chlorination level of the base flour up to 1.0 $\times$ . Cake volume then decreased slightly at the 2.0 $\times$  level of base, but the product was satisfactory in all visual respects. The figure also shows that the cake containing unchlorinated base flour plus 0.5 $\times$  lipids appears to be an anomaly, because it was significantly larger than either of the cakes next to it in the first horizontal row. Thus, the cake appeared to be out of sequence. Moreover, its oven performance was unique in that it expanded considerably during the heating cycle, virtually ballooning. The volume gradually decreased during cooling, but the final product was larger than expected.

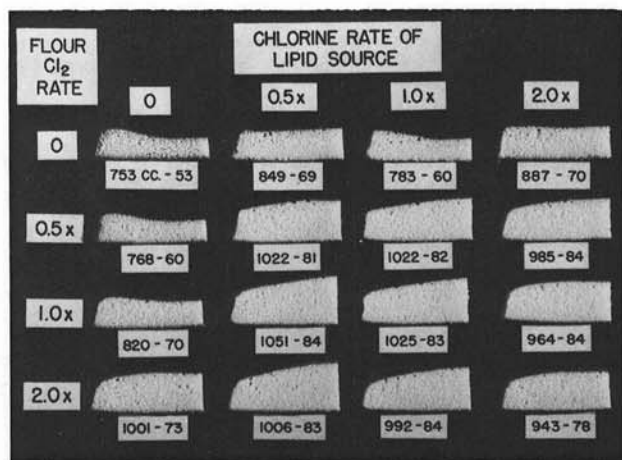


Fig. 3. Cross sections of cakes prepared from flours that had been sequentially chlorinated, defatted, and reconstituted, with interchange of lipids and bases in all possible combinations.

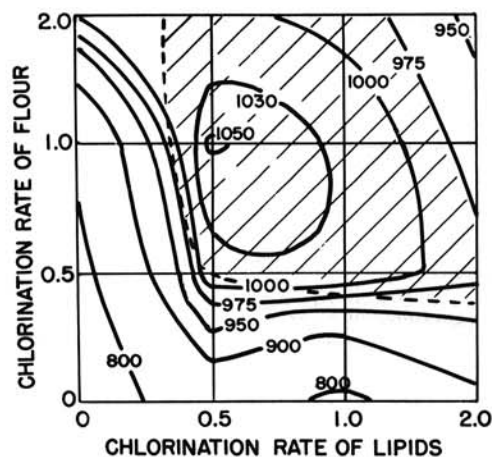


Fig. 4. Interpolated factor space showing cake volume responses for different combinations of free-lipid extracts and flour residues of differentially chlorinated flours. Shaded area represents limits of acceptable performance.

Batter expansions due to the use of 0.5 $\times$  lipids with both 0.5 $\times$  and 1.0 $\times$  bases were also noticeably larger than those for cakes made with whole chlorinated patent flour. These baking results suggest that the 0.5 $\times$  lipids had emulsification properties that increased the retention of leavening gases and that in the case of the unchlorinated base, the components have not been modified to the extent that the cake structure could support the potential volume. The possible implications of these observations are under investigation.

As the chlorination level of lipid source increased (1.0 $\times$  and 2.0 $\times$  columns), normal oven response and predictable products were obtained at each level of defatted base flour. Most notable in this series was the enhanced performance of defatted base from the high-chlorination treatment in combination with lipids from unchlorinated or low-level treatment sources.

If we consider these data (Fig. 3) as 16 points on a factorial response surface in two variables, contour lines may be interpolated and constructed to enable visualization of the system. Figure 4 shows the constructed surface describing cake volume responses for different combinations of the free-lipid extracts and flour residues of serially chlorinated flours. The shaded area defines the combinations of variables that should be satisfactory for both volume (975 cc or greater) and internal structure (scores of 80 or above), under the conditions of the experiment.

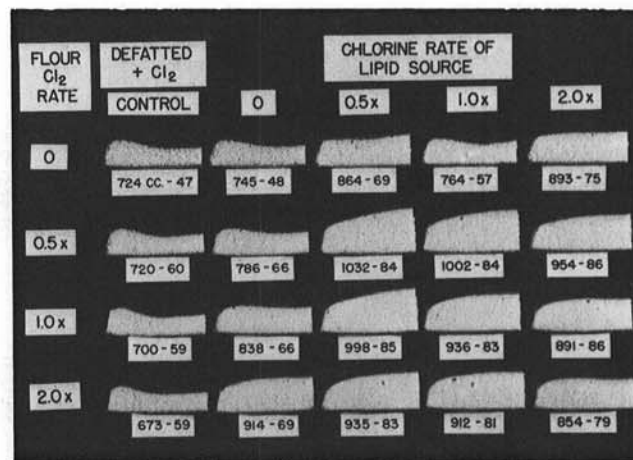


Fig. 5. Cross sections of cakes made from defatted and then serially chlorinated flours (control), and from those flours reconstituted in all combinations with lipids extracted from serially chlorinated flours.

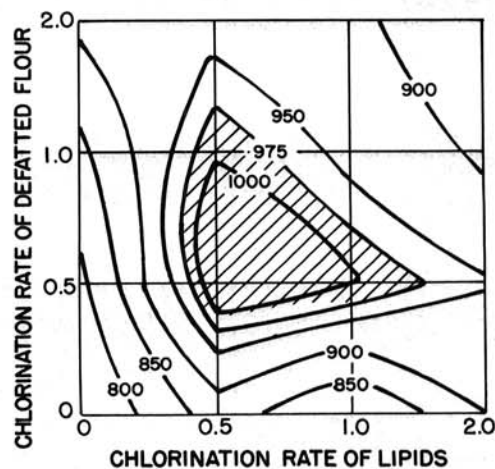


Fig. 6. Interpolated factor space showing cake volume responses for combinations of free lipid extracts from serially chlorinated flours and residues of flours that were defatted and then serially chlorinated. Shaded area represents limits of acceptable performance.

### Lipid Extraction Before Chlorination

The second portion of the study involved hexane extraction of free lipids from unchlorinated patent flour before treatment at 0.5×, 1.0×, and 2.0× levels of chlorine. Cake sections from the experiment are shown in Fig. 5. Baking results for the controls—the defatted flours after chlorination—are shown, along with the familiar interchange of lipids and bases. All the control cakes were failures, and were smaller than the corresponding cakes made with flour that had been defatted *after* chlorination (Fig. 2, middle column). When lipid extracts from flours chlorinated at different levels were added to base flours chlorinated *after* defatting, the array of responses was similar to that shown in Fig. 3 for the preceding set. The major difference was that most of the cakes in the latter test were smaller than their counterparts in the preceding test; hence, the number of acceptable combinations was also smaller. The absence of lipids at the time of chlorination did not prevent the flour from performing well in a high-ratio cake formulation, but the range of lipids with which the base could be reconstituted satisfactorily was reduced drastically.

Figure 6 is a graphic presentation of the response surface for the second experiment. The shaded area of overall acceptable performance is smaller than that shown in Fig. 4. Lipid extraction reduced the tolerance of the flour residue to the high rate of chlorination. The inflection of contour lines in the vicinity of the combination of 0.5× lipids plus unchlorinated base flour is an indication that functionality of that treatment was also greater than expected, owing to enhanced batter expansion during baking (Fig. 4).

### SUMMARY

The results of our study indicate that chlorination functionally modifies both extracted lipids and base flour. A compensatory relationship was found whereby the baking performance of highly

chlorinated base flour was improved by introduction of lipids from unchlorinated and from 0.5× and 1.0× chlorinated sources; to a lesser extent, the reverse was true. The baking potential of defatted base flour was greater when free lipids were present at the time of chlorination.

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