NONFAT DRY MILK FRACTIONS IN BREADMAKING. II. EFFECT ON OXIDATION REQUIREMENT[1]

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ABSTRACT

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Use of nonfat dry milk in the baking formula increased the potassium bromate requirement of dough and the dough's tolerance to excess potassium bromate. Both soluble and insoluble milk fractions increased the potassium bromate requirement. A dialyzable fraction of the solubles increased the potassium bromate requirement and appeared to buffer the requirement. A surface-response study with ammonium ion, phosphate ion, and potassium bromate as variables showed that, for all practical purposes, loaf volume was affected only by the concentration of ammonium ion. However, adding either ammonium ion or phosphate ion increased the potassium bromate requirement. The effects were additive; a combination of the ions required more potassium bromate than either alone. Thus, the potassium bromate requirement of NFDM comes from both the insoluble (protein) fraction and from ammonium and phosphate ions free or generated in the dough.

Adding a good baking quality nonfat dry milk (NFDM) to flour increases loaf volume of the bread produced (1). However, to obtain that volume increase, more potassium bromate (or other oxidant) is required. In addition to increasing the potassium bromate requirement, NFDM increases dough's tolerance to oxidant and thus partially prevents the deleterious effects of excess potassium bromate on loaf volume, crumb grain, and texture (2,3). Doughs containing NFDM and optimum potassium bromate gave loaves with higher volumes and better texture than did doughs containing optimum potassium bromate but no milk.

The study was undertaken to identify the fraction(s) of a good baking quality NFDM responsible for the increased potassium bromate requirement and potassium bromate tolerance of doughs containing NFDM.

MATERIAL AND METHODS

A commercial NFDM was fractionated by isoelectric precipitation and the soluble (whey) fraction was further fractionated by dialysis, as previously detailed (1).

The baking formula included: flour 100 g, sugar 6 g, salt 1.5 g, malt 0.75 g, shortening 3.0 g, NFDM (if any) 4.0 g, and yeast 2.0 g. A straight-dough procedure was used with optimum mixing time, absorption, and potassium bromate. All dry milk components were mixed with the flour thoroughly before any baking ingredients were added. Doughs were fermented 3 hr and proofed 55 min at 30°C, humidity 86%. Punching and moulding were mechanical. Baking time was 25 min at 218°C. Loaf volume was measured by rapeseed displacement within 3 min after loaves came from the oven. At least duplicate loaves were

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baked, and the standard deviation was 12 cc. Oxidation requirement was determined by subjective observation of the loaf and crumb.

Total and inorganic phosphates in the milk fractions (0.5 g) were determined by the methods of Fiske and Subbarow (4), as described by Hawk (5) and Pons *et al.* (6). Absorption was read at 720 nm.

Total phosphorus was determined by digesting samples in 50-ml Kjeldahl flasks with 3 ml sulfuric acid. After the organic matter was charred, several drops of 30% hydrogen peroxide were added and the sample was heated until the solution was colorless. The solution was heated 10 min after the last peroxide was added. After cooling, the sample was transferred to a 50-ml volumetric flask, and

TABLE I
Response Surface Design for Three Variables

Run Number	X_1[a]	X_2[b]	X_3[c]
1	−1	−1	0
2	1	−1	0
3	−1	1	0
4	1	1	0
5	−1	0	−1
6	1	0	−1
7	−1	0	1
8	1	0	1
9	0	−1	−1
10	0	1	−1
11	0	−1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

[a] X_1 = NH_4OH, −1 = 0.0%, 0 = 0.054%, and 1 = 0.108%.
[b] X_2 = H_3PO_4, −1 = 0.0%, 0 = 0.0769%, and 1 = 0.1538%.
[c] X_3 = $KBrO_3$, −1 = 0 ppm, 0 = 10 ppm, and 1 = 20 ppm.

TABLE II
Effects of Indicated Milk Fractions on the Oxidation Requirement of Bread[a]

	$KBrO_3$ Added		
Fraction	0 ppm	10 ppm	20 ppm
NFDM	−20	−10	0
No NFDM	−10	+ 5	+20
Insol	−10	− 5	+10
Sol	−20	0	+ 5
Sol_D	−10	+ 5	+20
Sol_{DZ}	0	0	+ 5
Insol + sol	−20	−10	0
Sol_D + sol_{DZ}	−10	0	+10
Insol + sol_D + sol_{DZ}	−20	−10	+10

[a] −20 indicates 20 ppm more potassium bromate needed, and +20 indicates 20 ppm less potassium bromate needed.

two drops of indicator (0.2% thymolphthalein in acetone) and 10 ml of 3.6*N* sodium hydroxide were added. The solution was acidified (1 drop of 10*N* sulfuric acid), diluted to volume with deionized water, and mixed. The inorganic phosphate procedure referred to above was then used to determine total phosphate.

Flour used was an untreated, commercial, hard winter wheat flour containing 11.9% protein and 0.40% ash. Response surface methodology, as described by Cochran and Cox (7) and Henika (8), was used with the design given in Table I. The equation for the response surface was:

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 + B_{13}X_1X_3 + B_{12}X_1X_2 + B_{23}X_2X_3$$

The B values were estimated by a computer program for multiple regression and nonsignificant terms were eliminated by stepwise deletion until a minimum mean square term was obtained. The program supplied a coefficient of

TABLE III
Phosphate ($PO_4^{\equiv}$) in Nonfat Dry Milk and its Fractions

Fraction	NFDM %	Total Phosphate[a] %	Free Phosphate[b] %
NFDM	100	100	100
Insoluble	36.1	24.9	2.14
Soluble	63.9	64.4	92.2
Soluble dialyzed	22.3	17.9	24.4
Soluble dialyzated	39.9	51.9	83.0

[a] Phosphate in 4 g NFDM = 0.1305 g.
[b] Free phosphate in 4 g NFDM = 0.0746 g.

TABLE IV
Loaf Volume Data Points for a RSM Study of Effects of NH_4OH, H_3PO_4, and $KBrO_3$[a]

$KBrO_3$ ppm	NH_4OH %	Loaf Volume (cc) when H_3PO_4 was 0.0000 %	0.0769 %	0.1538 %
0	0.00	...	825	...
10	0.00	837	...	800
20	0.00	...	818	...
0	0.054	895	...	898
10	0.054	...	900, 888, 903	...
20	0.054	880	...	858
0	0.108	...	908	...
10	0.108	907	...	923
20	0.108	...	915	...

[a] Equation for response surface $Y = 897.000 + 46.750X_1 - 5.125X_2 - 6.875X_3 - 23.125X_1^2 - 6.875X_2^2 - 7.735X_3^2 + 13.000X_1X_2$ where $X_1 = NH_4OH$, $X_2 = H_3PO_4$, and $X_3 = KBrO_3$. Coefficient of determination $R^2 = 0.97$.

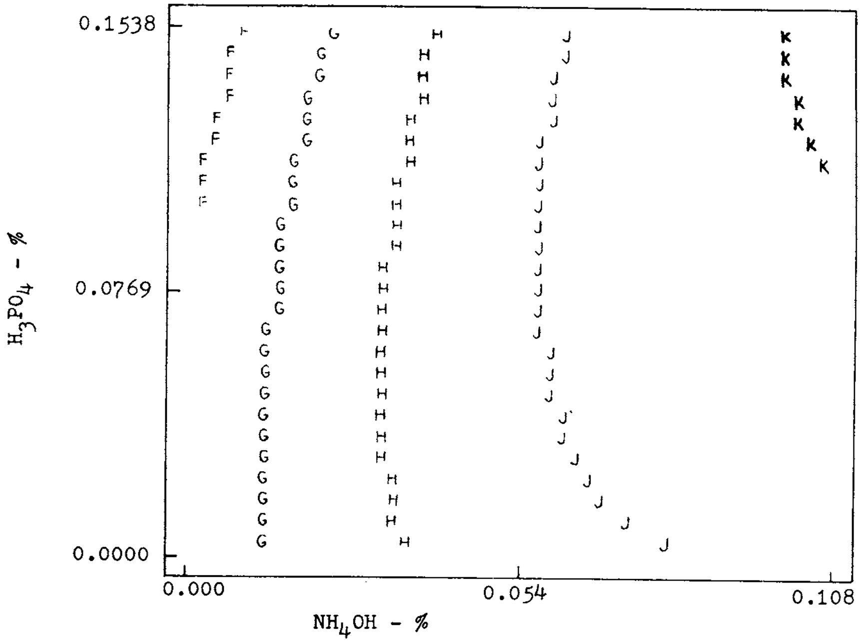

Fig. 1. Contour plot of loaf volume (F = 825, G = 850, H = 875, J = 900, and K = 925 cc) for H_3PO_4 and NH_4OH with $KBrO_3$ held at 0.0 ppm.

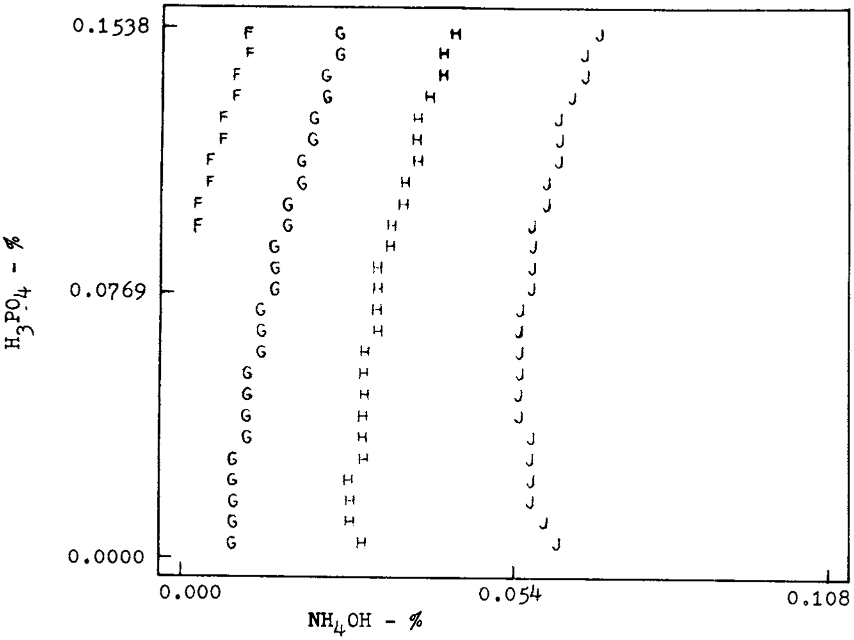

Fig. 2. Contour plot of loaf volume (F = 825, G = 850, H = 875, and J = 900) for H_3PO_4 and NH_4OH with $KBrO_3$ held at 10 ppm.

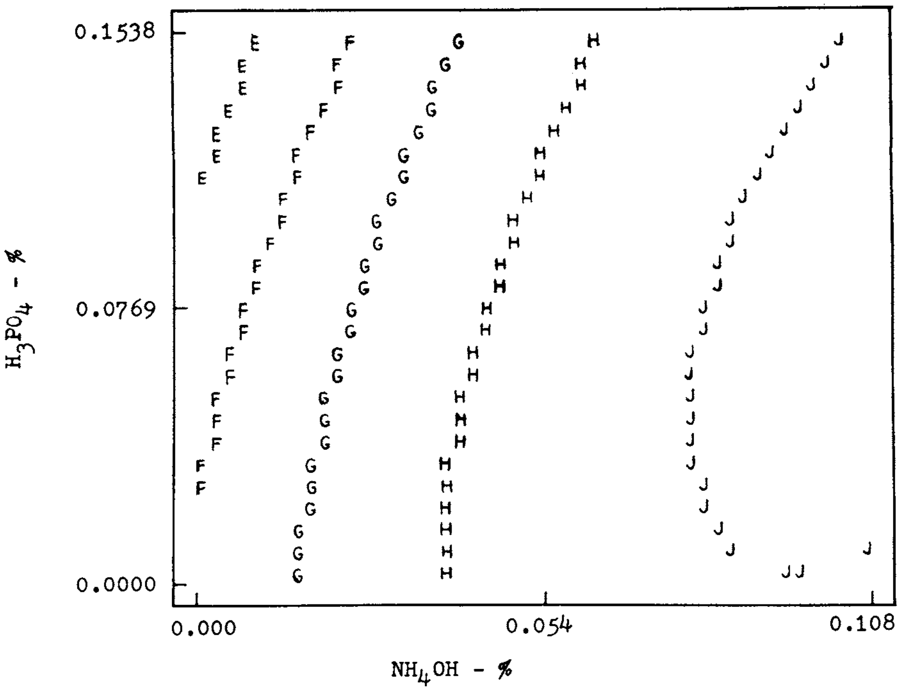

Fig. 3. Contour plot of loaf volume (E = 900, F = 825, G = 850, H = 875, and J = 900) for H_3PO_4 and NH_4OH with $KBrO_3$ held at 20 ppm.

TABLE V
Oxidation Characteristic Data Points for RSM Study of Effects of NH_4OH, H_3PO_4, and KBrO

		Oxidation Characteristic when H_3PO_4 was[b]		
$KBrO_3$ ppm	**NH_4OH %**	**0.0000 %**	**0.0769 %**	**0.1538 %**
0	0.00	...	2.5	...
10	0.00	2.5	...	4.0
20	0.00	...	4.5	...
0	0.054	3.0	...	2.0
10	0.054	...	2.5, 2.5, 3.0	...
20	0.054	4.5	...	3.0
0	0.108	...	2.0	...
10	0.108	3.0	...	3.0
20	0.108	...	3.5	...

[a] Equation for response surface $Y = 2.931 - 0.375X_1 - 0.250X_2 + 0.750X_3 + 0.346X_1^2 + 0.346X_2^2$ where $X_1 = NH_4OH$, $X_2 = H_3PO_4$, and $X_3 = KBrO_3$. Coefficient of determination $R^2 = 0.97$.

[b] A value of 3.0 equals optimum oxidation and each unit above (overoxidized) or below (underoxidized) is equivalent to 10 ppm $KBrO_3$.

determination (R^2) for each response. The equation was used to obtain contour plots of the response (Y) as a function of the variables.

RESULTS AND DISCUSSION

NFDM and certain of its fractions were added to flour and baked with three levels of potassium bromate in an effort to identify the fraction(s) that increase the potassium bromate requirement and give NFDM its buffering capacity. The data (Table II) are an appraisal of the need for more (−ppm) or less (+ppm) potassium bromate. From the data it appears that both the insoluble and soluble fractions required potassium bromate. When the soluble fraction was fractionated by dialysis, the sol_{DZ} fraction (material passing through the dialysis bag) required potassium bromate and also buffered the potassium bromate requirement.

Earlier work (9) tentatively identified phosphoric acid as an active agent in the dialyzable fraction of wheat flour. Because milk is rich in phosphorus, the sol_{DZ} fraction should contain phosphate ions. The NFDM and certain of its fractions were analyzed for total and free phosphate (Table III). As expected, the sol_{DZ} fraction was much higher in phosphate ion than were other fractions.

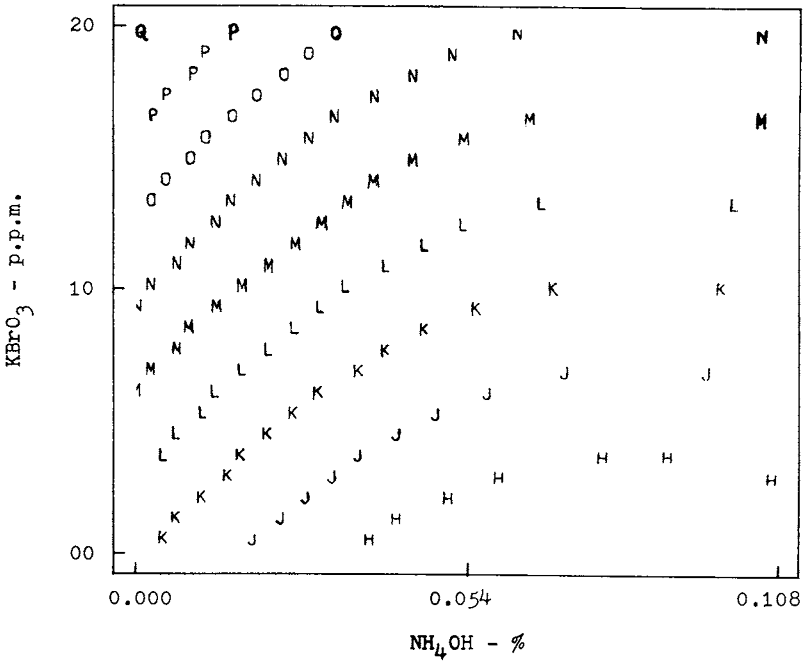

Fig. 4. Contour plot of oxidation appearance (G = 2.5, H = 2.75, J = 3.0, K = 3.25, L = 3.5, M = 3.75, N = 4.0, O = 4.25, P = 4.5, and Q = 4.75) for $KBrO_3$ and NH_4OH with H_3PO_4 held constant at 0.0%; 3.0 equals optimum oxidation and each whole unit above (overoxidized) or below (underoxidized) is equivalent to 10 ppm $KBrO_3$.

Bread baked with a formula containing no NFDM had a loaf volume of 812 cc, compared with 923 cc with 4% NFDM in the formula. The 111-cc increase in loaf volume could also be obtained using diammonium phosphate (1) instead of NFDM. A response surface experiment was used to study the effect of both ammonium and phosphate ions on the loaf volume and oxidation requirement of bread.

Loaf Volume

The loaf volumes of bread produced with added levels of ammonium hydroxide (0 to 0.108%, based on flour), phosphoric acid (0 to 0.153%, based on flour), and potassium bromate (0 to 20 ppm, based on flour) are given in Table IV. The response surface equation (see footnote, Table IV) has a coefficient of determination of $R^2 = 0.97$. Contour plots (Figs. 1–3) derived from the equation give loaf volumes as a function of the variables.

When potassium bromate concentration was held constant at 0.0 ppm, a relatively low loaf volume resulted (825 cc) for the entire concentration range of phosphoric acid studied. With increasing concentrations of ammonium hydroxide, loaf volume increased (850 to >900 cc). At the higher concentration of ammonium hydroxide studied, increased phosphoric acid concentration slightly increased loaf volume. Thus, it appears that ammonium hydroxide is the

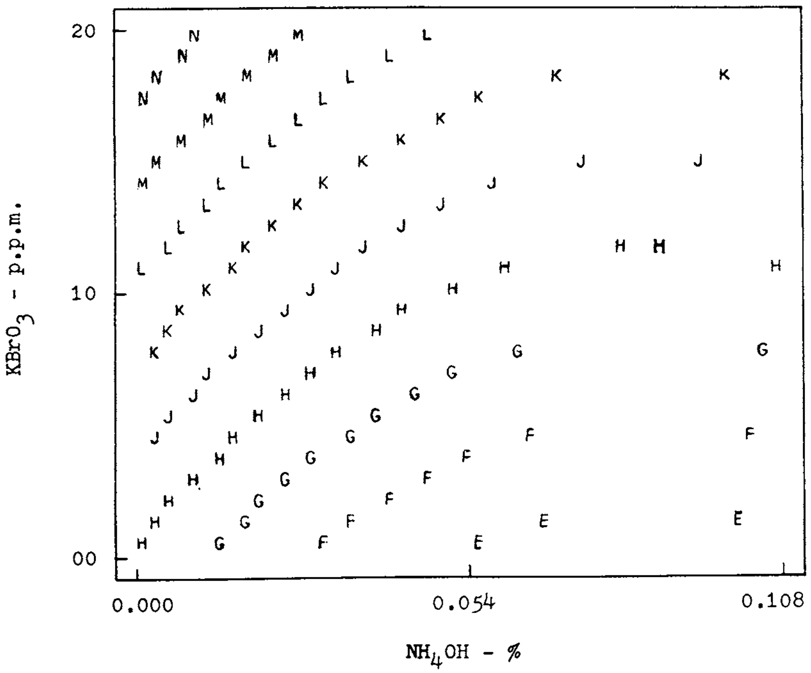

Fig. 5. Contour plot of oxidation appearance (E = 2.0, F = 2.25, G = 2.5, H = 2.75, J = 3.0, K = 3.25, L = 3.5, M = 3.75, and N = 4.0) for $KBrO_3$ and NH_4OH with H_3PO_4 held constant at 0.0769%; 3.0 equals optimum oxidation and each whole unit above (overoxidized) or below (underoxidized) is equivalent to 10 ppm $KBrO_3$.

factor affecting volume with a slight positive interaction with phosphoric acid. When potassium bromate concentration was held constant at 10 ppm, increasing phosphoric acid slightly decreased loaf volume. Adding ammonium hydroxide increased loaf volume from 825 to >900 cc. Similarly, when potassium bromate was held at 20 ppm, increasing phosphoric acid decreased loaf volume, and ammonium hydroxide increased loaf volume. Thus, for all practical purposes, loaf volume was affected only by the concentration of ammonium hydroxide.

Oxidation Characteristics

The oxidation appearance of bread produced under the above design is given in Table V. The response surface equation (see footnote, Table V) has a coefficient of determination of $R^2 = 0.97$. Contour plots (Figs. 4–6) derived from the equation give the oxidation appearance as a function of the variables.

When no phosphoric acid was added, increasing ammonium hydroxide required additional potassium bromate to maintain an optimum oxidation appearance (J). At the highest level of ammonium hydroxide, approximately 6 ppm potassium bromate was required. With phosphoric acid held at 0.0769, 4 ppm potassium bromate was required to give an optimum oxidation appearance with no added ammonium hydroxide in the system; increasing the ammonium hydroxide concentration again increased the potassium bromate requirement

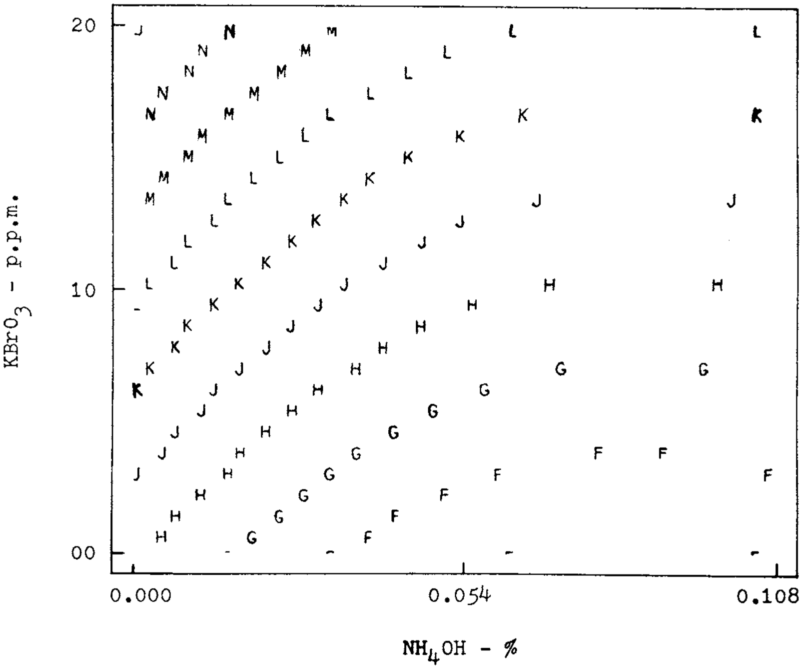

Fig. 6. Contour plot of oxidation appearance (E = 2.0, F = 2.25, G = 2.5, H = 2.75, J = 3.0, K = 3.25, L = 3.5, M = 3.75, N = 4.0, and O = 4.25) for $KBrO_3$ and NH_4OH with H_3PO_4 held constant at 0.1538%; 3.0 equals optimum oxidation and each whole unit above (overoxidized) or below (underoxidized) is equivalent to 10 ppm $KBrO_3$.

(15 ppm). Increasing the phosphoric acid concentration still more did not significantly alter the potassium bromate requirement.

Thus, it appears that adding either ammonium hydroxide or phosphoric acid to the system increases potassium bromate requirement. The effects appear to be cumulative, because a combination of ammonium hydroxide and phosphoric acid requires more potassium bromate than either alone.

To obtain an optimum loaf volume (>900 cc) and appearance (J), the ammonium hydroxide must be held high, phosphoric acid must be held at 0, and the potassium bromate must be held at about 5 ppm. Optimum loaves could also be obtained with more phosphoric acid if potassium bromate also was increased. Those results are for added ammonium and phosphate ions; they are not related to those ions already in flour. Adding 4% NFDM to the baking formula significantly increased the potassium bromate requirement (from about 5 to 20 ppm). The level of total phosphate ion expressed as phosphoric acid in milk (0.1305%, based on flour weight) would require 15 ppm potassium bromate, assuming adequate ammonium ion. However, the insoluble fraction of NFDM also required potassium bromate (Table II), so it seems safe to assume that not all of the phosphate in milk is free to give phosphate ions. Thus, it appears that the potassium bromate requirement of NFDM comes from both the insoluble (protein) fraction and from ammonium and phosphate ions free or generated in the dough.

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