ENHANCEMENT OF MATURING AGENTS BY METAPHOSPHATES[1]

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ABSTRACT

It was observed that several metaphosphates had substantial dough and bread improving properties at levels between 5 and 10 ppm. Either alone or in conjunction with commonly used oxidizing agents such as azodicarbonamide, potassium bromate, and acetone peroxide, they acted as flour and dough improvers or as enhancers for these maturing agents. It was found that the metaphosphates contribute to increased bread volume and especially to an improvement in grain and texture. The combinations tested (oxidizing agents plus metaphosphate) were effective in both the conventional and continuous baking processes, yielding superior results to those obtained from similar amounts of the oxidizing agents alone.

As part of another research project, we investigated the effectiveness of polyfunctional reagents such as metaphosphates on the cross-linking of starch. The intent was to evaluate the effects of 5 to 10 ppm sodium hexametaphosphate in sponge-baking tests by means of compressibility determinations. At these low levels, the compressimeter measurements showed no differences over the corresponding control. However, we noticed an overall improvement of the bread characteristics and decided to pursue this finding further.

The use of phosphates in general as additives to edible materials is well known and widely employed. A careful search of the literature, however, revealed only one reference with some similarity to our observations. Over 40 years ago, a French patent (1) was granted to add metaphosphates to doughs in amounts of 100–500 ppm to improve the flours used. These levels are well beyond the amounts tested in our studies. A specific point is made in this patent not to add metaphosphates at the low levels of 10–30 ppm, at which range bromate and per-salts are most effectively used.

MATERIALS AND METHODS

To evaluate the response of various metaphosphates at different levels, baking tests were carried out by the straight-dough "pup" method and the sponge-dough procedure. These tests[2] were conducted essentially as given in AACC Approved Methods (2), using 0.25% of a nonbromate, noniodate type of yeast food.

All the powdered agents were added to the flour in the form of a 10% premix throughout this series; and an even and uniform distribution in the flour was achieved by the use of an agitator.

Examples of metaphosphates tested in our baking experiments include sodium hexametaphosphate, sodium trimetaphosphate, sodium tripolyphosphate, metaphosphoric acid, SQ phosphate, and other similar phosphates which represent linear, polylinear, and polycyclic metaphosphate compositions with a

[1]Presented at the 60th Annual Meeting, Kansas City, Mo., Oct. 1975.

[2]The bread produced in these tests was graded by a modified A.I.B. scoring system. Over the years, this laboratory has been primarily concerned with maturing and bleaching compounds. Therefore, the modifications made for our purposes stressed the effects of these agents on grain and cell structure, crumb texture and color, and loaf volume.

wide range of molecular weights and which generally are described as powdered or amorphous, glassy materials. In Table I, several metaphosphates with some of their characteristics are presented. The nomenclature and classification are taken from literature available from the manufacturers of these different phosphates.

The Dalby (3) modification and technique were used for the Chopin extensimeter tests. Farinograph and mixograph tests were conducted according to AACC Approved Methods (2), except that the mixograms were made of flour-water doughs containing 2% salt. The mixograms were interpreted according to Pyler (4). The diastatic activity was measured by the pressuremeter method as outlined in the official AACC Approved Methods (2).

TABLE I
Nomenclature and Characteristics of Metaphosphates

Name	Formula	Structure	Molecular Weight	Properties
Sodium hexametaphosphate	$(NaPO_3)_n \cdot Na_2O$	Poly-linear	Approx. 1490	Anhydrous, glassy, amorphous product
Insoluble sodium metaphosphate	$(NaPO_3)_n$	Poly-linear	...	White, powdered material
Sodium trimetaphosphate	$(NaPO_3)_3$	Poly-cyclic	306	White, glassy product
Sodium tripolyphosphate	$Na_5P_3O_{10}$	Linear	368	White material

TABLE II
Baking Data of Various Metaphosphates
("Pup" Loaves—Straight Dough)

Additive	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	730	5.20	93.0
Sodium tripolyphosphate, 10 ppm	760	5.35	93.5
Sodium hexametaphosphate, 5 ppm	760	5.38	94.0
Sodium hexametaphosphate, 10 ppm	765	5.42	94.0
Sodium hexametaphosphate, 25 ppm	770	5.50	95.0
Insoluble sodium metaphosphate, 5 ppm	750	5.34	94.0
Insoluble sodium metaphosphate, 10 ppm	780	5.55	94.0
Sodium trimetaphosphate, 5 ppm	750	5.39	94.0
Sodium trimetaphosphate, 50 ppm	765	5.41	94.5
Sponge-Dough Procedure			
Control	2715	5.85	93.5
Insoluble sodium metaphosphate, 5 ppm	2780	6.03	94.0
SQ phosphate, 5 ppm	2800	6.18	94.0
Sodium hexametaphosphate, 5 ppm	2750	6.01	94.0
Sodium trimetaphosphate, 5 ppm	2835	6.22	94.0

RESULTS

Table II summarizes some of our bake results produced by the straight-dough and sponge-dough methods, using both a clear and a patent flour and various levels of different metaphosphates. The enhanced dough-handling properties and improved bread characteristics observed in the straight-dough "pup" method were substantiated in the sponge-dough process.

A series of other baking tests were carried out with combinations of a metaphosphate plus either azodicarbonamide (5,6), potassium bromate, chlorine dioxide (7), or acetone peroxide (8). In all our experimental baking tests, it was shown that all these improvers were compatible with any of the metaphosphates added. In this phase of the study, we were mainly concerned with conventional breadmaking processes, for the simple reason that in our laboratory the evaluation of new or improved products is first performed with the straight-dough and sponge-dough methods.

Generally, the treated bread in our tests was characterized by increased loaf volume, finer grain, softer texture, and improved exterior loaf characteristics. The improvement of the bread characteristics obtained with a metaphosphate-oxidizing agent combination was in most cases better than that observed for the

TABLE III
Baking Test Evaluation of Azodicarbonamide - Metaphosphate Combinations ("Pup" Loaves—Straight Dough)

Additive	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	740	5.28	93.0
ADA[a], 5 ppm	820	5.85	95.0
ADA, 10 ppm	845	6.05	95.5
ADA, 15 ppm	850	6.06	96.0
ADA, 5 ppm + SQ phosphate, 5 ppm	860	6.09	96.5
ADA, 10 ppm + sodium hexametaphosphate, 5 ppm	870	6.12	96.0
ADA, 15 ppm + sodium hexametaphosphate, 2 ppm	915	6.38	97.0
ADA, 15 ppm + sodium hexametaphosphate, 4 ppm	905	6.40	97.0
Sponge-Dough Procedure			
Control	2630	5.71	93.5
ADA, 10 ppm	2760	6.05	95.5
ADA, 10 ppm + insoluble sodium metaphosphate, 5 ppm	2850	6.13	96.0
ADA, 10 ppm + sodium trimetaphosphate, 5 ppm	2770	6.02	96.0
ADA, 10 ppm + sodium trimetaphosphate, 10 ppm	2760	6.01	96.0
ADA, 10 ppm + sodium hexametaphosphate, 5 ppm	2800	6.09	96.5

[a]Azodicarbonamide.

same oxidizing agent or the metaphosphate alone at the same treatment levels. Similarly, the doughs showed enhanced machining and handling properties.

Results of "pup" and sponge bakes using azodicarbonamide and various levels of metaphosphates are presented in Table III. As can be seen, most of the metaphosphates yielded a marked loaf-volume response and an improved grain and texture score. After extensive testing, it is our conclusion that sodium hexametaphosphate is superior to the other metaphosphates as an oxidizing agent enhancer.

For the last 13 years, azodicarbonamide[3] has been one of the maturing agents of choice in the milling and baking industries. These findings of generally improved bread characteristics from this combination treatment could lead eventually to the introduction of a new flour improver formulation (9).

In Table IV, baking test evaluations are reported for potassium halogenate and potassium halogenate combinations with different metaphosphates. In the straight-dough method, the use of 30 ppm of sodium hexametaphosphate did not result in an improvement over the lower levels tested. This table also shows the results obtained from 10 ppm potassium bromate or 5 ppm potassium iodate in combination with 5–10 ppm of several metaphosphates. Generally, we noticed that bread baked from metaphosphate-treated flour gave the appearance of additional whiteness which probably resulted from a finer cell structure in the bread.

We also observed in many cases that the appearance of a more open and somewhat coarser grain can be overcome with the addition of a metaphosphate. This finer and closer grain is due to the metaphosphate, since we could not see this property with the orthophosphates tested.

[3]A 10% azodicarbonamide premix with starch diluent is presently marketed under the name MATUROX®, a registered trademark of Pennwalt Corporation.

TABLE IV
Comparison of Potassium Halogenate - Metaphosphate Combinations ("Pup" Loaves—Straight Dough)

Potassium Bromate	Potassium Iodate	Insoluble Sodium Metaphosphate	Sodium Hexa-metaphosphate	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	...	...	...	730	5.05	93.5
10 ppm	...	...	...	795	5.60	95.0
10 ppm	...	...	5 ppm	830	5.75	96.0
10 ppm	...	10 ppm	...	825	5.77	95.5
10 ppm	...	...	30 ppm	820	5.70	95.5
		Sponge-Dough Procedure				
Control	...	...	...	2680	5.90	94.0
10 ppm	...	...	...	2820	6.25	95.0
10 ppm	...	5 ppm	...	2860	6.31	95.0
10 ppm	...	...	5 ppm	2870	6.29	95.5
10 ppm	...	...	10 ppm	2970	6.57	96.0
	5 ppm	...	...	2910	6.43	95.5
	5 ppm	5 ppm	...	2940	6.50	96.0
	5 ppm	...	5 ppm	2880	6.19	96.5

In Table V, results are given for a combination treatment of sodium hexametaphosphate with a mixture of bromate and azodicarbonamide in a 2:1 proportion[4]. The metaphosphate levels were varied between 20 and 100 ppm. Since the results changed little over this wide range, it can be concluded that this metaphosphate has a broad tolerance, at least in this particular system.

Table VI represents data obtained in the sponge-dough system for chlorine dioxide-metaphosphate mixtures. These combinations showed less pronounced improvement than the other oxidizing agent-metaphosphate mixtures tested[5].

The results obtained by the addition of 5 ppm metaphosphate in conjunction with 125 ppm acetone peroxide are presented in Table VII. As can be seen from the figures, there was quite an enhancement of all bread characteristics obtained by the addition of the metaphosphate.

A summary of results from a baking experiment simulating the continuous dough mixing process is given in Table VIII. These results were not obtained with the laboratory scale model of the Baker Process Do-Maker Unit, but with a special high-speed laboratory batch mixer. Fortmann *et al.* (10) described this equipment some years ago. Like the Brabender continuous laboratory mixer, the doughs cannot be developed, extruded, or handled continuously. But the final results are usually indicative of the performance that can be expected in the continuous process.

As can be noticed, in the continuous process when the optimum oxidation level is present, improvement is seen mainly in the grain and texture.

DISCUSSION

After having established the dough- and bread-improving properties of metaphosphates alone or in conjunction with commonly used oxidizing agents, we tried to find an explanation for our findings. As in the case of many powdered

[4]This mixture is used commercially at the bakery level under the name of WATOX®, a registered trademark of Pennwalt Corporation.

[5]At this point, it is proper to emphasize our observations made over many years of studying oxidizing agents. As everyone familiar with this field is aware, the degree of response of various oxidizing agents is different and also the effects obtained may vary with the flour grade and the baking procedure employed. Therefore, it should not be unexpected that similar results were obtained in this study testing various oxidizing agents, combined with different metaphosphates by the two baking processes mentioned.

TABLE V
Comparison of Potassium Bromate - Azodicarbonamide - Metaphosphate Combinations ("Pup" Loaves—Straight Dough)

Potassium Bromate	ADA	Sodium Hexametaphosphate	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	...	...	720	5.02	93.0
10 ppm	5 ppm	...	830	5.79	96.0
10 ppm	5 ppm	20 ppm	840	5.88	96.5
10 ppm	5 ppm	30 ppm	840	5.86	96.0
10 ppm	5 ppm	75 ppm	845	5.95	96.5
10 ppm	5 ppm	100 ppm	850	6.02	96.0

maturing agents, it is believed that there is no reaction with flour in the dry state.

It is evident from the chemical structure of the metaphosphates that they are not oxidizing agents as are most flour improvers or maturing agents. Therefore, we do not assume that sulfhydryl-containing substances in flour are involved in this improvement whereby they would be oxidized to disulfide linkages, as is the case with oxidizing agents (11).

TABLE VI
Baking Test Evaluation of Chlorine Dioxide - Metaphosphate Combinations (Sponge-Dough Procedure)

Chlorine Dioxide	Insoluble Sodium Metaphosphate	Sodium Hexa-metaphosphate	Sodium Tri-metaphosphate	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	...	...	...	2775	5.97	93.5
10 ppm	...	...	...	2800	6.13	96.0
10 ppm	5 ppm	...	...	2880	6.36	95.5
10 ppm	...	5 ppm	...	2780	6.05	96.0
10 ppm	...	...	5 ppm	2810	6.16	97.0

TABLE VII
Properties of Breads Baked with Acetone Peroxide - Metaphosphate Combinations (Sponge-Dough Procedure)

Acetone Peroxide	Insoluble Sodium Metaphosphate	Sodium Hexa-metaphosphate	Sodium Tri-metaphosphate	Volume cc	Specific Volume cc/g	Grain and Texture Score
Control	...	...	...	2650	5.70	93.0
125 ppm	...	...	...	2660	5.75	93.5
125 ppm	5 ppm	...	...	2780	5.95	96.0
125 ppm	...	5 ppm	...	2850	6.12	96.5
125 ppm	...	...	5 ppm	2795	6.05	96.5

TABLE VIII
Baking Data for Azodicarbonamide – Metaphosphate Combinations (High-Speed Batch Mixer)

Additive	Volume cc	Specific Volume cc/g	Grain and Texture Score
ADA, 30 ppm	2700	6.05	99.5
ADA, 30 ppm + sodium trimetaphosphate, 5 ppm	2680	6.02	100.0
ADA, 30 ppm + sodium hexametaphosphate, 5 ppm	2730	6.07	100.0
ADA, 30 ppm + insoluble sodium metaphosphate, 5 ppm	2740	6.19	100.5

For further elucidation, physical dough tests were carried out according to established procedures. The Chopin extensimeter test data are illustrated in Figs. 1 and 2. This instrument measures the extensibility of gluten as well as its gas-retaining powers. Two typical curves, one made with a baker's patent flour and the other with a clear flour, are shown in the figures. The treatment levels were 10 ppm sodium hexametaphosphate in each case, and the treated sample is compared with the untreated flour sample.

The treated flour curves show an increased resistance to expansion of the bubbles. The effects are slightly more pronounced in the clear flour, which is to be expected.

Farinograms were obtained for two patent flours containing about 9 ppm azodicarbonamide and the same flours with an identical dosage of azodicarbonamide plus 5 ppm sodium hexametaphosphate. It was evident from the curves that there was little difference between the two sets of farinograms, and in Table IX some of the farinograph data are summarized. The data for the two different flour samples, each one made with and without the addition of sodium hexametaphosphate, show practically no differences in mixing peak, mixing tolerance, and M.T.I.

Mixograph curves were obtained for a patent and clear flour, each containing 10 ppm sodium hexametaphosphate. The pattern of the mixograms indicated that the dough development stage and the range of stability were the same for the

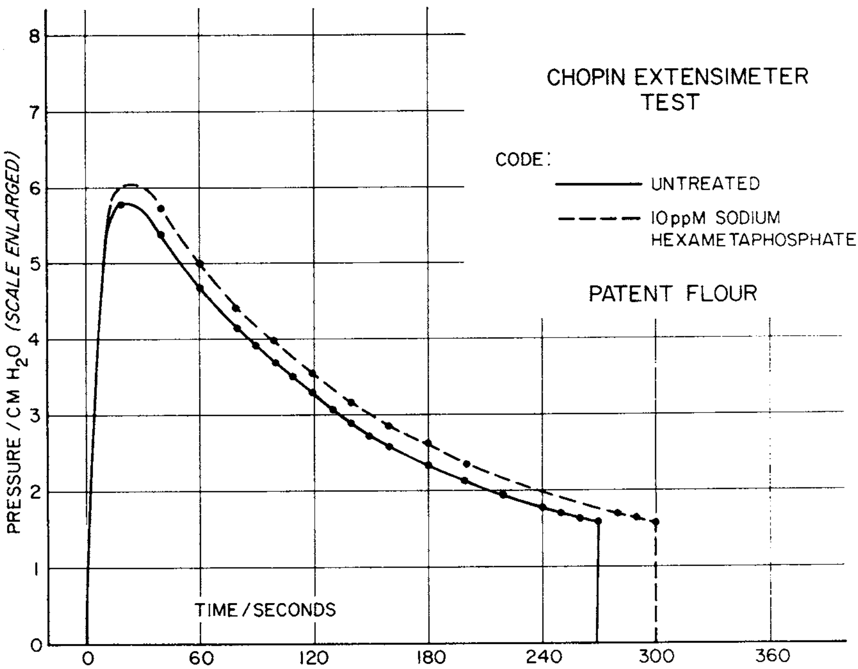

Fig. 1. Comparison of Chopin extensimeter curves for an untreated and hexametaphosphate-treated patent flour.

untreated control flour and the metaphosphate-treated sample. This would be in agreement with the farinograms discussed previously.

Sodium hexametaphosphate did not change or influence the rate of gas production by yeast, as measured by the manometric method. There was no difference between a flour containing 10 ppm sodium hexametaphosphate and the corresponding control flour without the metaphosphate addition.

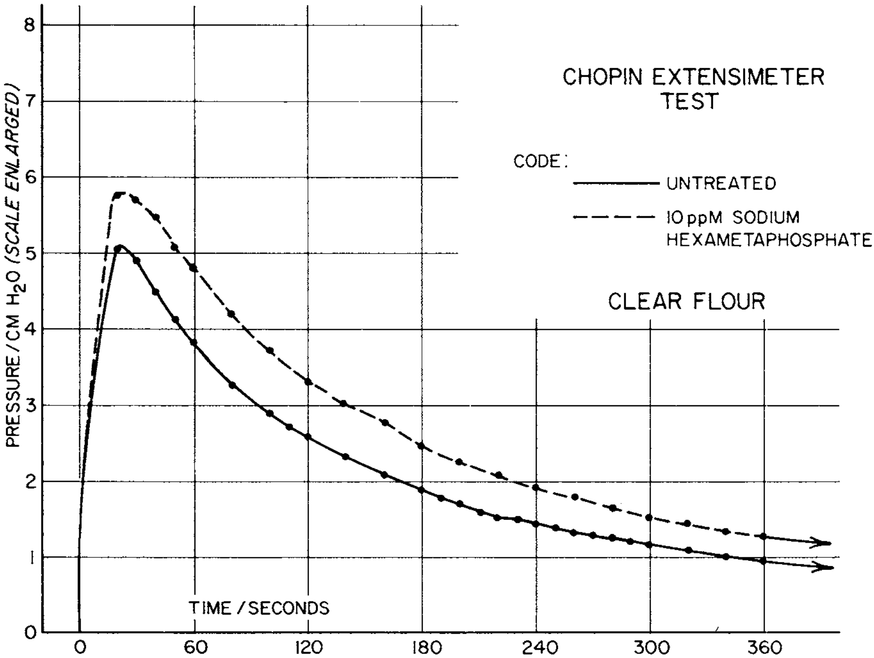

Fig. 2. Comparison of Chopin extensimeter curves for an untreated and hexametaphosphate-treated clear flour.

TABLE IX
Farinograph Data

Flour	Treatment	Mixing Peak min	Mixing Tolerance min	Absorption %	M.T.I.
Patent a	0.4 g ADA/cwt	6	13	60.3	20
	0.4 g ADA/cwt + 0.23 g Sodium hexametaphosphate/cwt	6	12.5	60.7	25
Patent b	0.4 g ADA/cwt	6.25	13.5	60.2	20
	0.4 g ADA/cwt + 0.23 g Sodium hexametaphosphate/cwt	6.25	13	59.9	20

The rheological properties of doughs made from flours treated with 10 ppm sodium hexametaphosphate did not reveal much difference over the untreated flour in physical dough testing methods. The baking results which showed that metaphosphates act as enhancers for the maturing agents tested may eventually be explained by a solubilization or chelating effect, or an independent starch cross-linking effect.

In 1972, Hoseney *et al.* (12) published a paper on fractions involved in the bromate reaction. Their conclusion was that, among the different flour fractions studied and required for the bromate reaction, a dialyzable part of the pH 6.1 fraction contained an entity which was identified as orthophosphoric acid. Whether this finding has any relation to our observations is an open question. As discussed previously, sodium or calcium orthophosphates did not demonstrate similar properties as found among metaphosphates.

Among the metaphosphates tested, we preferred sodium hexametaphosphate at levels between 5 and 10 ppm, as we noticed greater, more consistent, and more uniform overall flour and dough performance improvement obtained with this type of phosphate.

Literature Cited

1. DRAISBACH, F. Procédé pour l'amélioration des farines en vue de leur cuisson. French Patent 726,324 (1931).
2. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Approved methods of the AACC. Method 10-10, approved April 1961; Method 10-11, approved April 1961; Method 54-21, approved April 1961; Method 54-40, approved April 1961; and Method 22-11, approved April 1961. The Association: St. Paul, Minn.
3. DALBY, G. Flour bleaching and maturing agents. Proc. Amer. Soc. Bakery Eng. 27: 137 (1951).
4. PYLER, E. J. Baking Science and Technology. Siebel Pub.Co.: Chicago (1973).
5. JOINER, R. R., VIDAL, F. D., and MARKS, H. C. A new powdered agent for flour maturing. Cereal Chem. 40: 539 (1963).
6. TSEN, C. C. The reaction mechanism of azodicarbonamide in dough. Cereal Chem. 40: 638 (1963).
7. PARKER, H. K. Flour treatment with Dyox. Baker's Dig. 25: 30 (1951).
8. FERRARI, C. G., HIGASHIUCHI, K., and PODLISKA, J. A. Flour maturing and bleaching with acyclic acetone peroxides. Cereal Chem. 40: 89 (1963).
9. JOINER, R. R., and VIDAL, F. D. Metaphosphates as dough improvers. U.S. Patent 3840668 (1974).
10. FORTMANN, K. L., GERRITY, A. B., and DIACHUK, V. R. Factors influencing work requirement for mixing white bread dough. Cereal Sci. Today 9: 268 (1964).
11. SULLIVAN, B. Proteins in flour. J. Agr. Food Chem. 2: 1231 (1954).
12. HOSENEY, R. C., FINNEY, K. F., and SHOGREN, M. D. Functional (breadmaking) and biochemical properties of wheat flour components. X. Fractions involved in the bromate reaction. Cereal Chem. 49: 372 (1972).

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