BLEACHING AGENTS VERSUS POTASSIUM BROMATE IN BAKING WITH DRY MILK SOLIDS

by

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INTRODUCTION

Milk has been one of man's basic foods since prehistoric times. This was not without a reason; its nutritive value is such that it is used in an increasing number of foodstuffs thereby improving the product both nutritionally and physically. The manufacture of dry milk solids from whole milk has reduced it to a concentrated form without losing its valuable characteristics, and has facilitated its storage and handling.

The beneficial qualities of milk have not been overlooked by the baking industry during its rapid rise in the past half century. As a result dry milk solids are now used extensively in the breadmaking formulae. Its use introduces new problems to the commercial baker, many phases of which are not yet understood. It was to study these problems and to make dry milk solids an even more valuable product in the bakery, that the present investigations were undertaken.

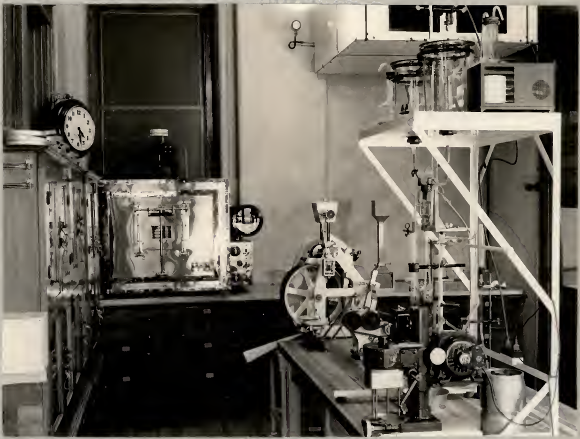


Fig. 1. View of the baking laboratory used in this investigation.

REVIEW OF LITERATURE

The date of the first use of milk as an ingredient in bread doughs is unknown, but it is probable that housewives have included this ingredient in bread for many centuries. Milk in bread was first studied scientifically from a nutritive viewpoint. Sherman et al (1921) found that bread made with milk instead of water produced improved growth and reproduction in rats when fed on a simplified diet.

Morison and Amidon (1923) cited Food Inspection Decision 188, issued by the United States Department of Agriculture in 1923, which defines milk bread in the following way:

> Milk bread is bread obtained by baking a wheat bread dough in which not less than one third (1/3) of the water ingredient has been replaced by milk or the constituents of milk solids in proportions normal for whole milk. It conforms to the moisture limitations for wheat bread.

These investigators fed bread made according to the above definition of milk bread to albino rats and also bread made with all of the water replaced by whole milk. The increased rate of growth of the rats fed on bread made entirely with milk over that made with one third of the water replaced by milk, showed conclusively the value of a liberal portion of milk in bread formulae.

Wihlfahrt (1931) cited the Federal Food Inspection decision issued in 1931 which read as follows:

> Milk bread is the product, in the form of loaves or small units obtained by baking a leavened and kneaded mixture of flour, salt, yeast, and milk or its equivalent (milk solids and water in the proportions normal to milk), with or without edible fat or oil, sugar and/ or other fermentable carbohydrate substance. It may also contain diastatic and/ or proteolytic ferments, and such minute amounts of unobjectionable salts as serve solely as yeast nutrients. The flour ingredient may include not more than 3 percent of other edible farinaceous substance. Milk bread contains, one hour or more after baking, not more than 38 percent of moisture.

The improvements in nutritive value of bread by the addition of dry milk solids was reported by Fairbanks (1928). White rats were fed three diets by the ad libitum method of feeding. The diets were: (1) milk free bread, (2) 6 percent dry milk solids in bread, and (3) 12 percent dry milk solids in bread. Sufficient water was fed in all of these diets. Fairbanks concluded that the addition of dry milk solids to bread increases the nutritive value of the bread. Bread with 12 percent of added dry milk solids had a higher nutritive value than did that with 6 percent dry milk solids. Dry milk solids in bread were declared to augment the use of liquid milk.

The manufacture of dry milk solids involves the application of heat treatment to the liquid milk.

Fairbanks and Mitchell (1935) studied the nutritive value of dry milk solids with special reference to the sensitivity of milk proteins to heat. They concluded that milk powders subjected to a temperature sufficiently high to produce a barely perceptible scorching are still as valuable as liquid skim milk as a source of energy in the animal body. Biological values of the proteins were established and it was found that they were lowered 8 percent in the "choice" roller and spray process which was due to partial destruction of cystine. At the scorching point the biological value of the proteins was only 72 to 80 percent of the original value due to the destruction of lysine. Digestibility was lowered at the scorching point although extreme scorching had little if any effect on the net-energy value.

The varying effects with different samples was a difficulty encountered in the early use of dry milk solids as an added constituent of bread doughs. Greenbank _et al_ (1927) found that milk which received a higher heat treatment in the drying process produced doughs of greater water-holding capacity and loaves of greater volume and better texture. Forty percent suspensions of dry milk solids were made up and checked for viscosity. Those milks treated at a high temperature (85°C. and above) gave distinctly higher viscosity determinations and were superior in baking quality. Milk given a lower heat treatment (65°C. and below) produced a binding effect on the bread doughs. This effect was attributed to the fact that these temperatures are not sufficiently high to coagulate the albumins.

Grewe and Holm (1928) studied the effects of several samples of dry skim milk, which had been subjected to varying degrees of preheating, on the baking quality of three flours obtained from the three major classes of bread wheats. A marked improvement in baking quality was obtained when preheating temperatures of 73°C., 83°C., 93°C., or 100°C. were used. There was only a slight difference between the latter two members of the series. They found that a preheating temperature of 50°C. gave the poorest results and of 63°C. the next poorest results.

Skovholt and Bailey (1931) found that preheating milks for a period of 30 minutes at temperatures of 77°C., 88°C., or 96°C. greatly improved the baking quality of the resulting powders. The absorption of the dough to which milk was added and the viscosity of the milk powder in water suspensions were not increased by preheating to 77°C. for 30 minutes. Marked increases were obtained in these respects when the milks were preheated to the higher temperatures. They found that the use of viscosity methods in determining baking quality of dry milk solids will not give reliable results when dealing with products which have received intermediate preheating treatments. Hydrogen-ion concentrations of dry milk solids in flour-water suspensions were not affected by preheating treatments. Electrical conductivity in water suspensions was only slightly different for dry milks receiving light or severe preheating treatments. The effect of depression of saccharogenic activity by added dry milk solids in a dough is not affected by the previous preheating treatment of the milk.

St. John and Bailey (1929a) studied the effect of dry milk solids on the fermentation and hydrogen-ion concentration of doughs. They found that production of total carbon dioxide in yeast leavened doughs was increased when dry milk solids was superimposed on the control formula. The effects were greater than those obtained by the use of fluid skim milk. The rate of increase of volume and total displacement of doughs were practically the same with and without added dry milk solids. This is an indication that loss of carbon dioxide from doughs was increased when dry milk solids were added. They demonstrated that the buffer action of dry milk solids was appreciable, as shown by the initial hydrogen-ion concentration of the freshly mixed doughs and by the relative rate of change in pH of the control and the milk-containing doughs.

The relation between the viscosity of non-sweetened condensed milk and baking quality was studied by Johnson and Ward (1936). They reported that the viscosity of superheated condensed milk is not necessarily an indication of baking quality. These investigators found that heat treatment seems to determine how condensed milk will react in bread making. Adequate heat treatment of the milk is necessary in order that the milk allows the proper absorption in bread doughs. This is also necessary so that the bread will show satisfactory texture, loaf volume, and oven spring. This heat treatment may or may not be given the milk in a way such as to increase the viscosity of the heated product. Increase in acidity of the milk either naturally or by direct addition of lactic acid allowed the development of considerable viscosity with a minimum of heat treatment, yet the baking results with viscous, acidified, heat treated milk were unsatisfactory.

Coombs (1938) studied factors which must be taken into consideration previous to the time of arrival of the raw milk at the manufacturing plant in order to make high quality dry milk solids. This investigator indicated that increase in acidity in raw milk is usually due to the action of organisms belonging to the streptococcus lactis group which is usually accompanied by an increased bacterial count. It is an indication of the manner in which the milk has been handled previous to delivery to the manufacturing plant. The acidity may be neutralized without injury to the dry milk solids produced but is considered a poor trade practice.

The effect of dry milk solids on the absorption of doughs and the plasticity of flour suspensions was investigated by St. John and Bailey (1929b). These workers showed that the addition of dry milk solids increases the water imbibing capacity of doughs as measured by the power input required in mixing. It was necessary to add about one unit of water by weight, for each unit of milk added to maintain the same plasticity in the dough as measured by the watt-meter and motor-driven mixer. Force required to extend a dough surface, as measured by the Chopin Extensimeter, likewise tended to decrease as the proportion of water was increased. This was observed with milk-free-doughs as well as those doughs which contained added dry milk solids. Extensibility, as measured with the Extensimeter was not substantially affected by the inclusion of 10 percent or less of dry milk solids in the dough.

Plasticity of flour-water dry milk solids suspensions was measured by Bingham and Murray's method (1923). It was found that mobility of such suspensions decreased with additions of dry milk solids and that the addition of one unit weight of water was necessary with each added unit weight of dry milk solids to retain the same relative mobility of suspensions.

Skovholt and Bailey (1932b) found that the magnitude of plasticity in Farinograph units decreased as the temperature increased on the same formula and same flour but in different mixes. They indicated that the inclusion of dry milk solids in dough increased the mixing time necessary to reach the maximum plasticity, and also that the inclusion of sodium chloride more than doubled the amount of additional water that could be added to reach a definite maximum plasticity when using dry milk solids. They observed that the amount of decrease in dough plasticity with extended mixing in a Farinograph gave a significant correlation with baking quality in a study of a series of milks. A good agreement was found in the rating of six of these milks by their plasticity curves when using two widely differing flours in doughs containing salt. Different ratings were obtained when salt-free and salt-containing doughs were compared. Absorption increases caused by milk were nearly the same regardless of the milk quality if the highest plasticity level attained was used as a measure.

In later work, Skovholt and Bailey (1935) observed that certain milk samples produced an effect on dough properties that was similar to the action resulting from the addition of minute amounts of proteases. They concluded that modification of the physical properties of a dough, involving the gluten, may occur even though the conventional biochemical methods fail to disclose appreciable quantities of those protein-split-products which are differentiated by these means.

Bohn and Bailey (1937) found that the addition of dry milk solids not fat markedly decreased the stress readings of a dough after mixing and increased the time of mixing required to reach the optimum development as indicated by the Farinograph. Good quality milk powders appeared to make a greater contribution to "strength" and gave higher stress readings than did poor milk powders. Mixing tolerance was benefited more by the good quality milk powders.

The investigation of Amidon (1926) appears to be the earliest publication on the effects of dry milk solids on the baking quality of flours. This investigator found, using amounts up to 10 percent, that dry milk solids gave an increase in loaf volume greater than the corresponding increase in dough weight. The crust color and character increased progressively with additional increments of dry milk solids. The presence of milk decreased the tendency of the break to "run wild". No effect on grain was observed until 8 percent were added. At this figure and at higher levels of added milk solids the milk appeared to detract from the quality of the grain, making it more open and coarser. The crumb color was "creamier" at this level, but it was also "brighter" and more lustrous. The flavor and taste of bread showed a gradual increase until a level of 7 percent dry milk solids was reached. Above this level the flavor decreased and the taste was less desirable. The texture was softer and more velvety with increasing quantities of added dry milk solids. The total score, which was the aggregate of all observed properties, increased progressively, on all flours used, with up to 7 or 8 percent of added dry milk solids. Above this level it tended to drop.

Working (1928a) studied the action of phosphatides in bread dough and observed that if 4 to 6 percent of dry milk solids were added to dough an improvement could be obtained by the addition of both a phosphatide and an oxidizing agent.

Grewe (1928) observed that the range of fermentation time over which good bread could be produced was increased by the addition of dry milk solids. The break and shred was also improved. This worker also observed that over-proofing was more detrimental in a milk-containing dough than in a milk-free dough. There was a greater increase in volume as a result of over-proofing a milk-containing dough than in a milk-free dough and with this increase in volume an increase in coarseness of grain resulted. The statement that the range of fermentation time over which a flour will give good bread was increased by the addition of dry milk solids was affirmed by a subsequent paper by Grewe and Holm (1928).

Skovholt and Bailey (1932a) compared the effects of additions of malt and dry milk solids and also the effects of additions of Arkady and dry milk solids. Flours of both hard winter wheats and hard spring wheats were used. They reported that malt and milk had a complementary effect on bread doughs. Malt added to doughs containing dry milk solids resulted in greater improvement than malt added to milk-free doughs. Milk added to doughs containing malt gave a more marked improvement than milk added to malt-free doughs that were milk-free. The improvement obtained by the use of Arkady under these conditions was much greater with the winter wheats than with the spring wheat flours. The improvement obtained by the use of added dry milk solids was much greater in doughs containing Arkady than in control doughs. Again a much greater percentage increase in improvement was obtained with the winter wheat flours than with the spring wheat flours. These results were obtained using both two and three hour fermentation periods.

Skovholt and Bailey (1933) observed while studying the susceptibility of bread milk to molds that added dry milk solids increased the hygroscopicity of both the bread crumb and the crust.

Skovholt and Bailey (1937) studied the effects of dry milk solids on fermentation reactions. They found that proteolytic activity in doughs, as judged by available methods which may quite possibly be inadequate, is not affected. Diastatic activity is retarded by the introduction of dry milk solids which reduces the hydrogen-ion concentration. There was no effect in buffered doughs. Gas production was accelerated in fermenting doughs if sufficient sugar was available. The milk-free doughs produced gas more rapidly during the earlier stages of fermentation but the doughs containing added dry milk solids produced gas more rapidly during the latter stages of fermentation. This was desirable to obtain the proper proof of the loaves. Yeast treated to inhibit growth was used in doughs and the results indicate that milk solids increased the activity of the zymase complex. This increase in activity seemed to result partially from an affected reduction of hydrogen-ion concentration.

Bohn and Bailey (1937) observed that a good grade of milk powder will improve the volume, texture, eating, and keeping qualities of bread. Poor milk powders, at a 6 percent level, may impair the physical and eating qualities of bread. The volume usually was decreased and the grain, though uniform, tended to be open and the cell walls thick.

Skovholt (1939) stated that since dry milk exerts a definite influence on the course of fermentation, certain changes in the procedure must be made. The dry milk obtained from the roller process of manufacture and the spray process have different mixing characteristics toward water. Dry milk exerts little if any influence on the proteolytic activity in doughs, reduces diastatic activity because of its acidity-reducing effect, lowers gas production because of its inhibition of diastases, accelerates yeast production in the presence of sufficient sugar, and retards the rate of water absorption. Corrective measures are designed to counteract these effects which should be thoroughly understood by the baker using dry milk.

Ofelt and Larmour (1940) studied the effect of dry milk solids on the properties of doughs. These workers observed that 6 percent added dry milk solids confers a high degree of tolerance toward the action of bromate on flours. Optimum results were obtained in baking at the 6 percent level of added dry milk solids. Tests showed that cysteine monohydrochloride exerts little effect on the final bread quality but does effect the mixing properties.

McCollum (1938) said, "So far as we know, the simplest, cheapest, and most effective way to improve the quality of bread is to introduce more milk solids not fat into its composition".

According to Bailey (1925) it appears that acidulation which results from treatment of freshly milled flour with chlorine serves to improve its baking qualities. Dunlap (1922) showed that the loaf volume of the chlorine treated flours immediately after treatment was approximately that of the untreated flour after being held in storage for 116 days. This observed increase in bread quality as measured by loaf volume and texture score might be due in part to the increased diastatic activity of the treated flour. Bailey and Sherwood (1924) investigated the baking quality of Kota wheat treated with chlorine. Not only was the loaf volume increased in proportion to the quantity of chlorine used, but the deep yellow color characteristic of flour milled from Kota wheat was largely dissipated.

Arpin (1921) did not observe any beneficial effect from treatment of flour with chlorine, basing his judgement upon the characteristics of the bread produced. An improvement in the baking quality of flour treated with chlorine was noted by Weaver (1922), and the fermentation period was reduced in consequence of such treatment. Treatment with nitrogen trichloride produced no increase in loaf volume, but it had a better texture. The color of the crumb of bread from flour so treated was much whiter, and sufficient treatment would result in the complete bleaching of the yellow coloring matter of the flour to white derivatives.

Stork (1922) stated that benzoyl peroxide will increase the water absorbing capacity of flour by 1 percent, and that the colloidal condition of gluten is favorably affected, resulting in larger loaf volume and better texture.

Dedrick (1924) wrote, "Flour a few weeks in storage becomes whiter and its baking qualities are improved. This fact, recognized, led investigators to attempt to accomplish this desirable effect by artificial means which would accomplish in a few seconds the same or better results than brought about by weeks or months of natural aging or bleaching. This process known as 'the aging and maturing process' is claimed to improve the quality of the flour as well as its color. Bleaching when properly carried out fixes the acidity and tends to carry away or overcome certain odors present in wheat."

"The coloring matter in flour is largely due to the fat or carotin. This substance is a yellowish pigment occurring in the various tissues of the wheat berry and other grains. This coloring substance is attacked and a chemical change brought about by gas, as that of nitrogen peroxide artificially produced by an electric arc, as the decolorizing agent. Chlorine gas and certain other chemicals as well as pure nascent oxygen are used as bleaching agents producing results similar to nitrogen peroxide."

"Too heavy a treatment of bleaching agent has been found to affect the strength and quality of the gluten. Overbleaching tends to affect the color also, giving a yellowish or bluish gray tint to the flour and increasing acidity. Bleaching accentuates the impurities in badly dressed flour. Low grades are only benefited by bleaching with certain reagents."

Dedrick (1924) stated that Agene improves the quality and gives greater loaf volume than the untreated flour, or natural aging, without changing the constituents of the flour. The action of Novadelox is gradual and takes place during 48 hours. If dough is made from treated flour within that period of time, no good bleaching results will be accomplished because the moisture in the dough counteracts the bleaching effect. Only an improvement in the baking qualities may result. The main claims of the Novadelox Process are: (1) bleaches pure white without a grayish or bluish shade, (2) matures the gluten, therefore, giving increased baking qualities to the flour, (3) will not overbleach the flour no matter what excess is applied, (4) Novadelox B had a strong sterilizing effect on flour, (5) application is very easy, (6) Novadelox B gives very good results on a low grade as well as patent flours. As the color of an aged flour is an index of its baking capacity so is the color of matured flour. Nitrosyl chloride is more effective in whitening flour than is chlorine, so that 0.5 percent of this reagent is necessary in Beta Chlora to have the color of the matured flour and its baking capacity run parallel, and in this sense parallel aged flour.

Micros (1926) reported the effect due to the action of chlorine on the basis of a pH change in the flour. Chlorine acted as an improver in addition to being a bleacher. When it was realized that aged flour was more acid than freshly milled flour it could be seen that chlorine treatment produced an immediate improvement in the baking value of flour. The treatment with chlorine increased the H-ion concentration of the flour so that maximum baking value was assured. This resulted in a shorter fermentation time, improved texture, and increased volume in the resultant loaf of bread. Chlorine treatment closely resembles natural aging since the flour is whitened and the full baking value developed.

Ferrari and Bailey (1929) stated that bleaching was the direct outgrowth of the demand for white flour. The earliest record of the use of chemical substances to whiten flour was the British patent number 2502, granted in 1879 to Beans. (Bailey, 1925). That the bleaching action of chlorine was not an entirely instantaneous process was significant. The greatest effect was produced at once, to be sure, but the bleaching action continued at a greater rate than could be accounted for by the natural bleaching of flour in storage. The bleaching action of nitrogen trichloride was similar to that of chlorine in that it was not instantaneous. In bleaching with Novadelox it seemed significant that all the flours, with their different initial carotin determinations were bleached about the same proportional amount in the same length of time. The flours bleached with the larger amounts of Novadelox did not maintain their advantage over smaller amounts after a comparatively long time.

Munsey (1935) stated that the bleaching powers of Novadelox is due to the oxidizing action of benzoyl peroxide which is converted into benzoic acid.

Smith (1937) investigated the effects of overbleaching flours, supplemented by baking tests. In general bread baked from untreated flour from the head of the mill had better shape, texture and volume than bread baked from that from the bottom of the mill. It was upon the latter that Agene had such remarkable effects, giving bulky and lively doughs, and loaves of better texture, color, and much increased loaf volume. With over-treatment the dough became "short" and lacked elasticity, giving loaves whose surfaces became fissured and cracked. Novadelox had no discernible improving properties upon doughs although baked loaves in many instances appeared to be improved in texture. Therefore, the question of how far bleaching could be carried without over-improvement occurring, does not arise. Like

Agene, Beta Chlora's improving effects appeared more marked upon lower grade flour. Its bleaching and improving effects were similar to Agene.

King et al (1937) in a report of the United States Department of Agriculture bread flavor committee reported that taste was more important than odor in determining preference in bread flavor. There was no significance to the judgement on odor or taste when bleaching treatment was employed.

According to Swanson (1938) the action of benzoyl peroxide is due to the fact that it releases its oxygen which reacts with the carotin of the flour. Chlorine not only unites with the carotin but also with other constituents, particularly the fat. The nitrosyl chloride hastens oxidation. The maturing effect is fastest with the use of chlorine mixed with nitrosyl chloride, somewhat less with nitrogen trichloride, and the least with nitrogen peroxide and benzoyl peroxide. In the final destruction of yellow color the last two are rated equal with the first two. Bleaching agents increase the hydrogen-ion concentration. The reaction of nitrogen peroxide with water results in the formation of nitrous and nitric acids. Benzoic acid is formed from benzoyl peroxide. Hydrochloric acid is formed from the reactions of chlorine and its compounds. There is also an increase in hydrogen-ion concentration in the unbleached flour and the hydrogen-ion concentration also increases in the bleached flour in the months following the bleaching treatment.

Bogert (1938) stated: "Carotenoid is defined as a nitrogen-free polyene pigment, constituted wholly or chiefly of a long acyclic chain of carbon atoms united in an uninterrupted sequence of double bonds, which system functions as a chromophore. These pigments vary in color from a bright yellow to a deep red, or even a violet, or a dark blue, the depth of shade increasing with the number of conjugations in consecutive union, and decreasing as the double bonds are saturated. The color therefore is determined by the number and distribution of the conjugated double bonds and by the number and character of the atomic groupings in immediate union therewith." Substitutions into the ionone ring at both extremities of the molecule of B-carotene has no marked effect on the color.

Bogert further states, "Spectroscopic observations have been of great importance in the study of the carotenoids and in determining their constitution. Ordinarily, the more conjugated double bonds there are united in immediate and uninterrupted sequence, the longer the wave length of the maximum light extinction, provided that the molecular structure remains the same general type. However any chemical change in the chromophoric portion of the molecule is promptly reflected in the absorption spectrum."

The carotenoids in nature are found either free or combined and usually in colloidal solution in the lipoids. The carotenoid alcohols thus function much the same way as other alcohols in the formation of fats and waxes. Like common fats which can be technically hardened, these pigment waxes can be catalytically hydrogenated smoothly to colorless products which closely resemble ordinary fats and waxes. Iodine chloride will add to all the olefin bonds and hence can be used to corroborate the results of hydrogenation.

Baker (1922) reported traces of nitrites in flour treated with nitrogen trichloride. Traces of chlorine were also found in the fats of the flour when higher rates of treatment were applied. Bailey (1925) believed that the carotene of flour is oxidized into one of its colorless derivatives when the peroxidase of the flour liberates active oxygen from benzoyl peroxide which in turn oxidizes the carotene. Catalase of the flour on the other hand, is detrimental to the extent that it liberates molecular oxygen, which form of oxygen is without effect on carotene.

Blish and Sandstedt (1927) investigated factors affecting interpretation of experimental baking tests. These workers concluded that under modern industrial conditions the use of oxidizing agents may be the chief factor which determines bread characteristics, aside from differences in such items as wheat varieties and flour grades. Gluten is profoundly affected by minute quantities of oxidizing agents such as are universally used by both miller and baker. The effect is usually one of stimulation and development where the treatment is properly controlled, but if excess of oxidizer is used the result is detrimental, producing symptoms of more or less advanced "age".

Geddes and Larmour (1933) studied some aspects of the bromate baking test. They found that natural aging of flour resulted in a decrease in potassium bromate response. Potassium bromate does not influence the rate nor the amount of carbon dioxide production in bread doughs but modifies their gas retaining capacity indicating that it exerts a direct or indirect action on the gluten proteins.

Flohill (1936) investigated the effect of chemical flour improvers on the proteolytic action in relation to the gas-retaining capacity of fermenting doughs. This investigator concluded that an optimum condition for proteolytic action in the dough was absolutely necessary for best baking results. If through overbleaching or overtreatment with chemical improvers, too much of the proteolytic enzymes have been destroyed, tough and unyielding doughs will be obtained resulting in unsatisfactory bread.

Balls and Hale (1936) found that, during the process of dough fermentation, the action of a proteinase in flour changes the colloidal properties of the wheat proteins. The change in the flour will eventually show itself in the properties of the gluten. Proteinase usually produces first a coagulation of the protein; later the coagulated material is broken down and perhaps ultimately destroyed. If this rule holds for flour, in the first phase of proteinase action the gluten would probably become more tenacious; in the second phase it would be broken down to a thinner, more nearly liquid material. It is evident that a very small amount of the proteolytic enzyme is ample to produce the desirable effects. It is now possible to give a satisfactory explanation of the changes that take place in the quality and behavior of flours after they have been bleached or stored in air. This alteration of flour is due to a dimunition of the proteolytic activity brought about by the activator of the proteinase. Similar effects are produced when the oxidant is added to the dough as a "bread improver."

Geddes and Larmour (1933) directed attention to a possible ionic effect on the gluten proteins by bromate whereby the gas-retaining capacities of the gluten was increased. Working (1928b) explained the action of oxidizing action on flour as a liberation of phosphatides which in turn reacted favorably upon the gluten. Geddes (1930) suggested that the benefits derived from the use of bromate may arise from the oxidations of certain germ components believed to be detrimental, presumably the phosphatides. On the basis of experimental results Kosmin (1934) concluded that gluten quality as governed by "improving agents" is a function of the degree of coagulation effected by these agents. Potel (1934, 1935) published studies dealing with the effects produced by small quantities of various chemicals on the plastic properties of flour pastes. This writer concluded that there exists in wheat flour a substance associated with the gluten complex which is susceptible to oxidation and reduction. In a series of three papers, Jorgensen (1935, 1936) discredited the phosphatide and "electrolyte" theories and presented considerable data to support his contention that the benefits derived from bromate and other agents which behave in like manner in bread doughs are the direct result of protease inhibition.

MATERIAL AND METHODS

For the investigation, ten-bushel samples of Tenmarq, Chiefkan, and Turkey wheats were carefully selected on the basis of pureness of variety, protein content, and test weight. The protein content of each was approximately equal (Table 1) thus making the samples desirable for a quality study from a variety standpoint. This flour protein range (12.2 percent to 12.6 percent) was desirable for the dry milk solids, bleaching and potassium bromate investigations because it approximates the average figure for flour from these three varieties as grown in Kansas during 1939.

Table 1. Analytical data for ten-bushel lots of wheats and flours milled therefrom.

Variety	Test wt. of wheat	Moisture		Protein*		Ash*		Baking absorption
		Wheat	Flour	Wheat	Flour	Wheat	Flour	
	lb.	%	%	%	%	%	%	%
Tenmarq	59.2	10.4	12.7	13.6	12.2	1.234	.399	61.6
Turkey	56.7	10.5	13.3	13.6	12.5	1.748	.441	60.8
Chiefkan	58.9	11.9	13.3	13.8	12.6	1.[illegible]62	.412	62.7

*15 percent moisture basis.

The Chiefkan sample was produced at Corbin, Kansas; the Tenmarq at Isabel, Kansas; and the Turkey at Oberlin, Kansas. The protein content of the wheats were almost identical with only a .4 percent difference in the flours after milling on the commercial size Kansas State College 65-barrel mill. The wheat was washed, tempered to 16 percent moisture for 20 hours, and the moisture content at the first break roll controlled by the addition of steam when necessary.

The flours were not bleached, packed in 48 pound cloth sacks, and placed immediately in a cold room at 40 - 42°F. to prevent aging as much as possible. It was found by probing the various sacks that the protein content varied within the sack so the top half of all sacks were mixed for 20 minutes in a large steel-barrel mixer. The remainder formed the second mix. The straight flour was used throughout the experiment.

The No. 1 sack of Turkey was thoroughly mixed in the steel mixer and used as a check sample for laboratory control. It appeared in each day's bake during the investigation.

It appeared advisable to give a brief description of the chemical bleaches used in these investigations. Nitrogen trichloride is used in flour bleaching under the trade name of Agene. It is a hazardous substance and has a tendency to explode if placed under the right conditions. This danger has been minimized with the development of equipment designed to permit it to be used with greater safety. Nitrogen trichloride is produced by passing chlorine gas through a solution of the Agene salt. (Sulphate of ammonia). Hypochlorous acid is formed in the first stage of the reaction. In the second stage hypochlorous acid reacts with the Agene salt to form a nitrogen trichloride. The equations for the two stages of the reaction are given below:

First stage:

$$\underset{\text{chlorine}}{6Cl_2} + \underset{\text{water}}{6H_2O} \rightleftarrows \underset{\text{hydrochloric acid}}{6HCl} + \underset{\text{hypochlorous acid}}{6HOCl}.$$

Second stage:

$$\underset{\text{hypochlorous acid}}{6HOCl} + \underset{\text{ammonium sulphate}}{(NH_4)_2SO_4} \rightleftarrows \underset{\text{nitrogen trichloride}}{2NCl_3} + \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{water}}{6H_2O}.$$

When the nitrogen trichloride comes in contact with the moisture in flour the following reaction occurs:

$$\underset{\text{nitrogen trichloride}}{NCl} + \underset{\text{water}}{3H_2O} \text{ (flour)} \rightleftarrows \underset{\text{ammonia}}{NH_3} + \underset{\text{hypochlorous acid}}{3HOCl}.$$

Hypochlorous acid, a relatively unstable compound, is thought to release oxygen which reacts with carotene to form a colorless derivative of the pigment. The exact nature of this reaction, however, is not entirely known.

As indicated by the reaction only one half of the chlorine is used in producing nitrogen trichloride.

Beta Chlora is the trade name given to the compound containing 99.5 percent of anhydrous chlorine and 0.5 percent of nitrosyl chloride. This bleaching agent is very widely used, due probably to its rapid reacting properties.

The chemical reactions for the process are shown below:

1. Action of anhydrous chlorine:

Cl_2	+	H_2O (flour) $\rightleftarrows$	HCl	+	$HOCl$
chlorine		water	hydrochloric acid		hypochlorous acid

2. Action of nitrosyl chloride:

$NOCl$	+	H_2O (flour) $\rightleftarrows$	HNO_2	+	HCl
nitrosyl chloride		water	nitrous acid		hydrochloric acid

Hypochlorous acid is thought to react on the carotene of flour in the same manner as described in the Agene process. Chlorine also has been thought to combine directly with the carotene. The exact reaction of nitrous acid, which is very unstable, with carotene is not entirely known but upon decomposition is thought to act as a catalyst to hasten oxidation.

Beta Chlora has in the past been used more for its maturing effect rather than for color improvement. For this reason Novadelox, noted for its whitening properties, is used in conjunction with Beta Chlora in many modern mills.

Benzoyl peroxide is a solid organic peroxide which is now used in the milling industry under the trade name of Novadelox. Formerly it was named Novadelox B. It is a mixture of benzoyl peroxide (16 parts), dicalcium sulphate (80 parts), and magnesium carbonate (4 parts). Dicalcium sulphate and magnesium carbonate are used to reduce the inflammability and spontaneous ignition properties of Novadelox. Benzoyl peroxide was used in the bleaching of fats and oils previous to its introduction into the milling industry. It has a slower reaction time than other bleaches used in this study.

The reaction of Novadelox on flour is shown below:

$$C_6H_5\overset{O}{C}-O-O-\overset{O}{C}C_6H_5 + H_2O \text{ (flour)} \rightleftarrows 2C_6H_5COOH + O$$

benzoyl peroxide water benzoic acid oxygen

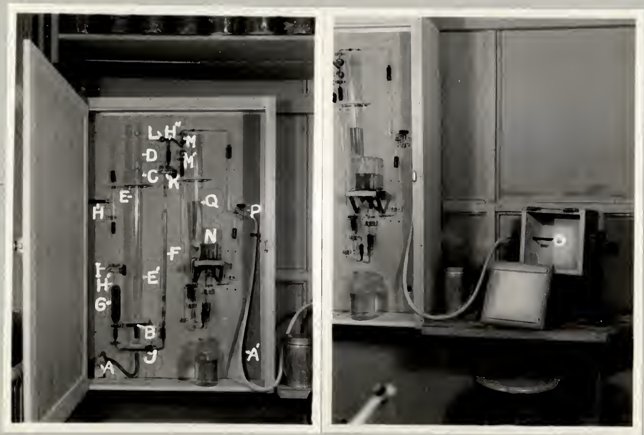
The oxygen is thought to react with the carotene of flour to form one of its colorless derivatives.

A special bleaching apparatus (Plate I and Fig. 2) designed by J.E. Anderson of the Kansas State College Milling Department was constructed in connection with this investigation in order to bleach a small sample of flour with gas with considerable accuracy.

One of the chief difficulties encountered in experimental bleaching is the measuring of small volumes of gas at uniform pressure. Securing a uniform flow of gas to the agitator constitutes another troublesome problem. This apparatus was built with the object of eliminating these difficulties as much as possible.

The chlorine or Beta Chlora as the case may be was supplied from the storage cylinder (A) or (A') containing liquid chlorine to a tall upright glass cylinder (B).

PLATE I



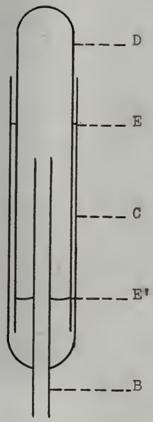


Fig. 2. A diagram of the cylinder containing gas under a slight pressure.

A diagram of cylinder (B) is shown in Fig. 2. The outside tube (C) was sealed to tube (B) which was of small bore used for admitting and withdrawing gas. To complete the chamber, tube (D) was inverted inside tube (C) and outside tube (B). Water (E and E') saturated with chlorine was used as a seal between tubes (C) and (D). As gas entered the chamber through tube (B), tube (D) was buoyed up by the gas which was held under a slight pressure equal to 11 to 13 inches of water above atmospheric pressure.

The measuring device consisted of a burette (F) graduated to deliver the volume of gas required to secure the desired amount of bleach on the basis of one pound of flour. The calibrations gave direct readings in grams of Agene per barrel of flour and ounces of chlorine per barrel of flour when one pound of flour was bleached. The graduate was calibrated by allowing the water to drain from the tube and the amount removed taken as the volume of gas which passes in. The water was drained out rather than poured in to eliminate the error in volume of the water which clings to the burette upon draining.

Calculations of volumes of gas used to bleach a one pound flour sample.

1. Beta Chlora:

Cl_2 (from Beta Chlora) used at rate of 1 oz. per bbl. (196 lbs.)

Molecular weight $Cl_2 = 70.91$

1 lb. = 453.5 g.

1 oz. = $453.5 \div 16 = 28.34$ g.

1 lb. flour requires $28.34 \div 196 = .1446$ g. Cl_2.

$\frac{.1446}{70.91} = \frac{x}{22{,}400}$ $x = 46$ cc. (standard temperature and pressure)

$46 \times \frac{760}{731} \times \frac{298}{273} = \underline{\underline{51}}$ cc. at 25°C. and 730 mm. pressure

2. Agene:

3 moles Cl_2 (from Agene) $\rightleftharpoons$ 1 mole NCl_3

$3 \times 70.91 \rightleftharpoons 120.38$

Agene rate of 1 g. per bbl.

$1 \div 196 = .0051$ g. per lb. of flour

$\frac{3 \times 70.91}{120.38} = \frac{x}{.0051}$ $x = .009$ g. Cl_2 required

$\frac{.009}{70.91} = \frac{x}{22,400} = 2.85$ cc. (standard temperature and pressure)

$2.85 \times \frac{760}{730} \times \frac{298}{273} = \underline{\underline{3.32}}$ cc. (at 25°C. and 730 mm. pressure)

The burette (F) was connected directly with the water reservoir (G). The water reservoir (G) had access either to the air pressure line (H') or the atmospheric pressure by means of the two-way stopcock (I). Lowering or lifting of the column of water in the burette (F) was controlled by stopcock (J). The flow of gas to and from the burette (F) was regulated by two-way stopcock (K). The difference in air pressure sufficient to raise the column of water was controlled by stopcock (L). The direction of the flow of gas upon leaving burette (F) was regulated by stopcocks (M and M'). M and M' determined whether the gas bubbled indirectly through the Agene salt solution in the inverted beaker (N) and then to the agitator (O) through the two-way stopcock (P), or passed directly to the agitator (O) through stopcock (P). The first gave an Agene bleach; the latter a Beta Chlora bleach. About one eighth of the Agene salt solution in the beaker (N) was replaced by fresh solution from reservoir (Q) following each bleach to maintain a uniform concentration.

In the process of bleaching with Beta Chlora, the gas was released from Beta Chlora storage cylinder (A) into glass cylinder (B). The charge was measured by placing reservoir (G) under atmospheric pressure and lowering the water from the top of burette (F) through stopcock (J). To remove the charge, stopcock (K) was reversed, reservoir (G) placed under air line pressure at (H'), and the rate of flow into air pressure line (H'') controlled by stopcock (J). The time of removal of the charge was approximately one half the total time of agitation. The charge was then passed directly through stopcock (M and P) to agitator (C).

In bleaching with Agene the process of measuring into and removal from burette (F) of the charge was the same as for Beta Chlora except the Agene storage cylinder (A') was used. Upon removal from burette (F) the charge was passed through stopcock (M'), bubbled through inverted beaker (N), and forced through stopcock (P) into agitator (C).

Novadelox, a powdered solid, was applied directly to the flour and mixed in agitator (C).

Agene (nitrogen trichloride), Beta Chlora (nitrosyl chloride), and Novadelox (benzoyl peroxide) were used in amounts of one half, one (full), one and one half, two, three, and four times the bleach used by many commercial mills as normal for straight flour. The exact amount of bleach added in each case was based upon the following figures as the normal or full bleach: Agene, 3.00 g. per bbl. of flour (196 pounds); Beta Chlora, .75 oz. per bbl. of flour; Novadelox, .40 oz. per bbl. of flour.

A one-pound sample (a sufficient amount to bake duplicate 200 g. mixes and make control tests) was bleached. The Agene and Beta Chlora bleached flours were agitated approximately four minutes in direct contact with the incoming mixture of bleaching gas and air. Since Novadelox is a solid and more difficult to distribute uniformly it was mixed for eight minutes in the agitator.

After bleaching, the flours were stored uniformly in airtight cans at a room temperature of approximately 70°F. for 10 days. It is believed that Agene and Beta Chlora complete their reaction in two to three days while Novadelox, to give full effect, requires one week. Thus, this storage procedure was employed to insure the completion of all reactions and to give a uniform storage treatment.

In order to reduce possibilities of error in bleaching, carotene ($C_{40}H_{56}$) determinations were made on the flours. The apparatus used was a Wilkens-Anderson K.W.S.Z. photometer (Shrewsbury, Kraybill, and Withrow, 1938). In this determination 20 g. of flour were digested in 100 cc. of water saturated butyl alcohol for 15 minutes, filtered for six minutes, and readings taken on duplicate portions of the filtrate. (Binnington and Geddes, 1939). The apparatus was calibrated against B-carotene. All transmittancy readings were obtained in a 10 cm. cell and converted into carotene equivalents of B-carotene in parts per million (p.p.m.) by means of a table based upon the specific transmissive index (k) for carotene of 1.6632 in normal butyl alcohol. This value was determined by Binnington, Sibbitt, and Geddes (1938).

The potassium bromate used throughout this investigation was chemically pure and of reagent quality. The solutions were made to such a concentration that 10 cc. would deliver the increment desired for a dough containing 200 g. of flour. Potassium bromate ranging from zero to 7 mg. in 1 mg. increments per 100 g. of flour was used.

The term dry skim milk was formerly applied to the product made from drying skim milk but is gradually disappearing from literature dealing with human foods. At present this product is being referred to as "dry milk solids". The dry milk solids used in this investigation was manufactured by the spray process. In this process the liquid skim milk is sprayed under high pressure into a drying chamber where the fine spray comes in contact with a current of heated air. This causes rapid evaporation of the moisture from the milk and leaves the solid matter behind in the form of tiny particles which fall to the bottom of the chamber.

Dry milk solids may be defined as the product resulting from the removal of fat and water from whole milk. It contains not over 1.5 percent butterfat and not over 5 percent moisture. Dry milk solids normally contain approximately 51 percent lactose, 37 percent protein, 8 percent minerals, 1 percent fat and 3 percent moisture. In other words it includes all the constituents of whole milk except fat and water in full amount in a concentrated form.

The dry milk solids used in this investigation was analyzed to insure the writer that a representative sample was being used. The composition of the sample was 36.31 percent protein, 8.27 percent minerals, 2.70 percent moisture and 1.05 percent fat. Lactose for which there was no available means of measurement was taken as the difference and amounted to 51.67 percent. All values were very near the figures of an average sample so the sample was considered representative.

A baking study of preliminary nature using dry milk solids of known baking quality gave comparable results with the dry milk solids used in this investigation. Six percent dry milk solids were used in these studies as a result of the findings of Ofelt and Larmour (1940). According to Wihlfahrt (1935), the Baker's Weekly (August 13, 1932) clarified the interpretation to be placed on the federal government definition of milk bread given earlier in this report by the following statement in regard to dry milk solids: "When using dry milk solids the weight to be used is equal to 0.1001 times the water absorption. This dry skim milk (dry milk solids) must be used jointly with a weight of 0.0497 times the water absorption in butter or a corresponding equivalent in butterfat". Based upon 60 percent water absorption 6 percent dry milk solids must be contained to meet government requirements. The water absorption of the flours used in this investigation exceeded 60 percent and only 6 g. per 100 g. of flour of dry milk solids were used so the bread could not be classed as "milk bread" according to the federal definition. In addition the required equivalent of butterfat was not used. The powdered milk was thoroughly mixed with the flour before adding any of the other baking ingredients.

The baking formula used was as follows:

Flour	200 g.
Water (distilled)	as required
Yeast	4 g.
Sugar	12 g.
Salt	3 g.
Shortening (hydrogenated vegetable)	6 g.
Malt syrup (120°L.)	0.5 g.
Dry milk solids	as indicated
Potassium bromate	as indicated

Baking absorption was determined by a method developed by Karl F. Finney of the Hard Wheat Quality Laboratory, Kansas Agricultural Experiment Station. This method required 20 g. of flour. All ingredients shown in the above formula (dry milk solids 6 percent, potassium bromate 2 mg.) were included. Water added with the ingredients equaled 50 percent absorption. Additional water to reach the optimum absorption was added during mixing. The doughs were mixed to optimum consistency. They were fermented for three hours according to the regular baking schedule. The doughs were observed when ready for panning. If not at the optimum consistency an estimate was made of the amount to be added or subtracted from that actually used. This corrected value was used in the baking trials.

The figure for absorption was increased 1 percent for each percent of dry milk solids used. The absorption figure for each variety was held constant throughout regardless of treatment of flour. Doughs were mixed with a Swanson-Working mixer in a bowl containing four pins at 66 revolutions per minute to an optimum consistency determined by observation. The mixing time was held constant for each variety. Two hundred grams of flour went into each mix. The doughs were divided into two equal portions after mixing, fermented, and proofed at 86°F. and 90 percent relative humidity. The fermentation pans were covered during fermentation. The total fermentation time was three hours during which time the doughs were punched twice, at intervals of 105 minutes (1st punch), and 50 minutes (2nd punch). Twenty-five minutes later they were panned into tall form A.A.C.C. pans and then proofed for 55 minutes. A National pup sheeting roll was used for punching and the molding was done on a Thompson Model A laboratory molder. Proof heights of the loaves were measured upon removal from the proof cabinet. The loaves were baked at 430°F. for 24 minutes in a specially designed Despatch oven (Finney and Barmore, 1939) with a rotating hearth. The oven was humidified to prevent dead dull crust colors. Loaf volumes were measured immediately after the loaves were taken from the oven. The figures for loaf volumes given in the tables are averages of at least four loaves from two bakes. Some mixes were triplicated where necessary to insure accurate results. To be considered accurate the two loaves obtained from one mix could not differ more than 25 cc. from each other. In addition the averages of loaves from each mix had to agree within 20 cc. The loaves were cut the following morning in order to grade the internal characteristics and to obtain a photograph for a permanent record. The method used by Karl F. Finney was used in calculating the total baking scores shown in the tables. The loaf characteristics were weighted in the following manner.

Loaf volume score equals (actual loaf volume - 300 cc.) x .1 .

Grain score equals (score on basis of 100) x .3 .

Texture score equals score made on basis of 22 points.

Color score equals (score on basis of 100) x .1 .

The baking laboratory in Fig. 1 (p. 2) was air-conditioned and the temperature was held between 76 to 78°F.

EXPERIMENTAL RESULTS

The optimum potassium bromate requirements for the three flours investigated are given in Table 2. The baking results and carotene determinations are shown in Tables 3 to 5 and representative loaves are presented pictorially in Figs. 3 to 8. Plates II to IV show the results graphically.

Table 2. Baking data showing optimum $KBrO_3$ requirements of three flours when baked with and without 6 percent dry milk solids. (D.M.S.)

	Tenmarq	Turkey	Chiefkan
No milk	2 mg.	2 mg.	2 mg.
With D.M.S.	4 mg.	6 mg.	4 mg.

Table 3. Data on Tenmarq flours given various treatments when baked with or without 6 percent dry milk solids (D.M.S.).

Treatment		Carotene in p.p.m.	No milk: Loaf volume in cc.	No milk: Total baking score	6 percent D.M.S.: Loaf volume in cc.	6 percent D.M.S.: Total baking score
No treatment		1.64	620	80.1	736	92.7
		—				
Agene						
g. per bbl.	1.5	.64	660	87.1	770	98.2
	3.0	.40	663	86.7	778	101.2
	4.5	.24	666	88.0	792	102.4
	6.0	.20	670	88.9	796	103.2
	9.0	.14	682	89.3	790	105.3
	12.0	.06	690	90.4	802	105.1
Beta Chlora						
oz. per bbl.	.38	.92	633	80.6	750	95.4
	.75	.68	620	79.6	724	93.2
	1.13	.60	621	81.5	736	94.7
	1.50	.52	634	85.1	735	96.0
	2.25	.51	668	87.8	745	98.5
	3.00	.50	665	86.3	766	100.6

Table 3. Continued.

Novadelox						
oz. per bbl.	.20	1.09	618	79.3	738	95.0
	.40	.75	633	81.9	747	97.5
	.60	.49	648	83.6	749	98.6
	.80	.34	655	82.8	757	98.8
	1.20	.20	656	85.2	771	101.7
	1.60	.16	668	89.5	791	104.3
$KBrO_3$						
mg. per 100	1		729	96.6	852	106.8
g. flour	2		745	95.9	864	113.2
	3		723	92.0	870	114.5
	4		698	90.1	912	119.9
	5		667	88.3	899	116.2
	6		650	84.9	858	112.2
	7		-	-	852	111.8

Table 4. Data on Turkey flours given various treatments when baked with or without 6 percent dry milk solids (D.M.S.).

Treatment		Carotene in p.p.m.	No milk: Loaf volume in cc.	No milk: Total baking score	6 percent D.M.S.: Loaf volume in cc.	6 percent D.M.S.: Total baking score
No treatment		2.55	607	72.8	638	68.9
Agene g. per bbl.	1.5	1.68	607	73.4	650	74.0
	3.0	.97	616	73.7	652	76.5
	4.5	.76	614	74.7	654	78.5
	6.0	.70	620	79.9	656	81.0
	9.0	.54	630	81.9	664	81.8
	12.0	.42	628	82.4	678	86.0
Beta Chlora oz. per bbl.	.38	1.61	608	72.4	632	71.7
	.75	1.40	618	76.4	622	73.1
	1.13	1.24	628	76.4	627	73.5
	1.50	1.15	626	76.3	627	76.0
	2.25	1.11	630	80.4	626	74.0
	3.00	1.07	648	81.9	636	76.0

Table 4. Continued.

Novadelox oz. per bbl.	.20	1.78	617	74.8	648	72.6
	.40	1.20	616	74.0	655	77.8
	.60	.81	628	78.9	649	77.2
	.80	.71	625	77.6	663	80.6
	1.20	.34	635	81.0	657	82.1
	1.60	.23	651	83.9	673	85.1
$KBrO_3$ mg. per 100 g. flour	1	-	751	97.6	739	96.8
	2	-	840	107.0	788	101.9
	3	-	818	104.4	838	109.2
	4	-	816	102.3	879	114.3
	5	-	762	97.0	915	117.3
	6	-	760	95.4	932	119.0
	7	-	-	-	884	115.3

Table 5. Data on Chiefkan flours given various treatments when baked with or without 6 percent dry milk solids (D.M.S.).

Treatment		Carotene in p.p.m.	No milk: Loaf volume in cc.	No milk: Total baking score	6 percent D.M.S.: Loaf volume in cc.	6 percent D.M.S.: Total baking score
No treatment		2.07	557	62.1	606	66.4
Agene g. per bbl.	1.5	1.29	580	66.2	635	72.9
	3.0	.79	580	68.6	637	75.5
	4.5	.67	581	70.0	638	76.0
	6.0	.65	591	72.6	639	79.7
	9.0	.61	590	75.9	642	79.7
	12.0	.53	605	79.2	642	80.5
Beta Chora oz. per bbl.	.38	1.38	577	66.6	617	69.5
	.75	1.17	587	69.3	624	72.9
	1.13	1.15	587	70.7	616	72.1
	1.50	1.13	585	72.0	614	74.2
	2.25	1.01	595	76.2	615	74.0
	3.00	.96	605	78.2	620	76.2

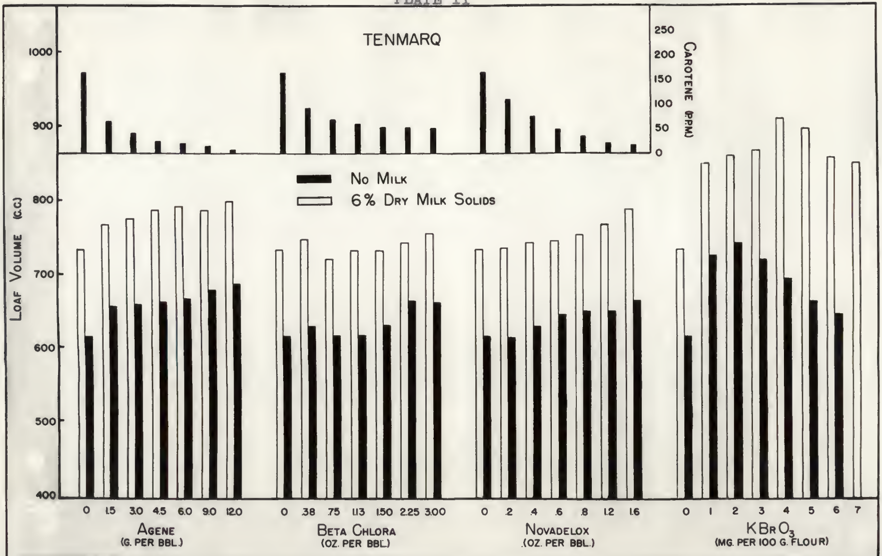
Table 5. Continued.

Novadelox oz. per bbl.	.20	1.18	570	66.6	625	73.5
	.40	.80	575	67.5	624	75.7
	.60	.51	584	70.2	627	76.1
	.80	.39	592	71.5	639	78.3
	1.20	.31	608	73.0	640	78.2
	1.60	.30	608	72.2	645	78.7
$KBrO_3$ mg. per 100 g. flour	1	-	613	76.3	639	79.8
	2	-	652	86.9	685	86.7
	3	-	634	86.3	702	94.1
	4	-	628	84.6	712	95.7
	5	-	618	82.6	712	94.2
	6	-	573	79.1	712	95.0
	7	-	-	-	712	95.0

EXPLANATION OF PLATE II

Variations in loaf volume produced by bleaching agents or potassium bromate on Tenmarq flour doughs containing no dry milk solids and 6 percent dry milk solids. The effect of various kinds and rates of bleach upon carotene is also shown.

PLATE II

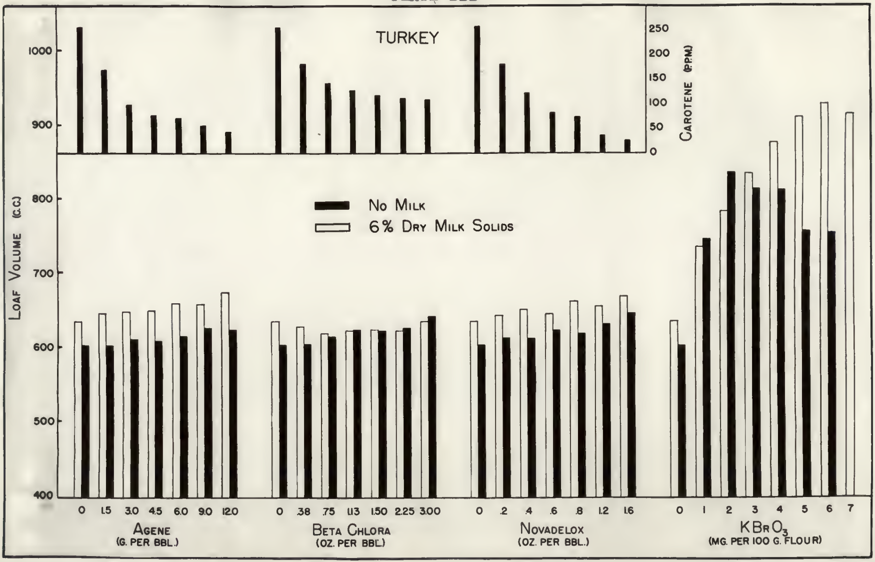


TENMARQ
Loaf Volume (c.c.)
1000
900
800
700
600
500
400
Carotene (p.p.m.)
250
200
150
100
50
0
No Milk
6% Dry Milk Solids
0 1.5 3.0 4.5 6.0 9.0 12.0
Agene
(g. per bbl.)
0 .38 .75 1.13 1.50 2.25 3.00
Beta Chlora
(oz. per bbl.)
0 .2 .4 .6 .8 1.2 1.6
Novadelox
(oz. per bbl.)
0 1 2 3 4 5 6 7
$KBrO_3$
(mg. per 100 g. flour)

EXPLANATION OF PLATE III

Variations in loaf volume produced by bleaching agents or potassium bromate on Turkey flour doughs containing no dry milk solids and 6 percent dry milk solids. The effect of various kinds and rates of bleach upon carotene content are also shown.

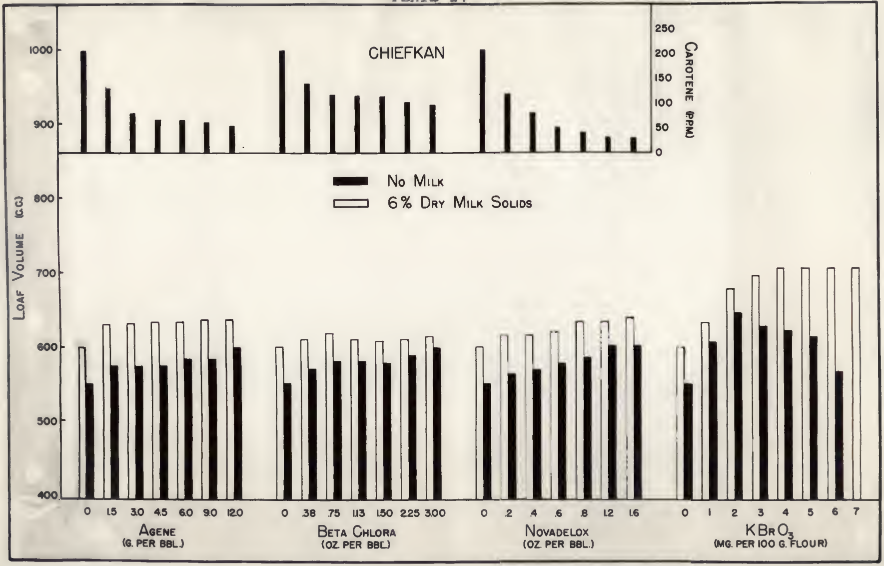
PLATE III


TURKEY
1000
900
800
700
600
500
400
LOAF VOLUME (C.C.)
250
200
150
100
50
0
CAROTENE (P.P.M.)
No Milk
6% Dry Milk Solids
0 1.5 3.0 4.5 6.0 9.0 12.0
AGENE
(G. PER BBL.)
0 .38 .75 1.13 1.50 2.25 3.00
BETA CHLORA
(OZ. PER BBL.)
0 .2 .4 .6 .8 1.2 1.6
NOVADELOX
(OZ. PER BBL.)
0 1 2 3 4 5 6 7
$KBrO_3$
(MG. PER 100 G. FLOUR)

EXPLANATION OF PLATE IV

Variations in loaf volume produced by bleaching agents or potassium bromate on Chiefkan flour doughs containing no dry milk solids and 6 percent dry milk solids. The effect of various kinds and rates of bleach upon carotene content are also shown.

PLATE IV


CHIEFKAN
Loaf Volume (c.c.)
1000
900
800
700
600
500
400
Carotene (p.p.m.)
250
200
150
100
50
0
No Milk
6% Dry Milk Solids
0 1.5 3.0 4.5 6.0 9.0 12.0
Agene
(g. per bbl.)
0 .38 .75 1.13 1.50 2.25 3.00
Beta Chlora
(oz. per bbl.)
0 .2 .4 .6 .8 1.2 1.6
Novadelox
(oz. per bbl.)
0 1 2 3 4 5 6 7
$KBrO_3$
(mg. per 100 g. flour)

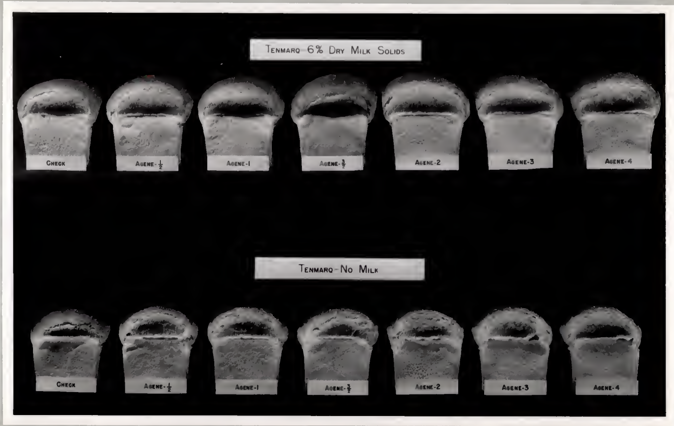


Fig. 3. The effect of dry milk solids in relation to varying treatments of Agene bleach on loaf exterior. Tenmarq wheat flour.

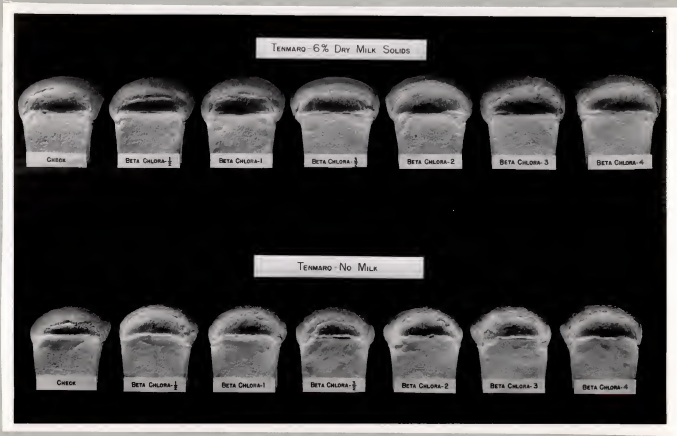


Fig. 4. The effect of dry milk solids in relation to varying treatments of Beta Chlora bleach on loaf exterior. Tenmerq wheat flcur.

Fig. 5. The effect of dry milk solids in relation to varying treatments of Novadelox bleach on loaf exterior. Tenmarq wheat flour.

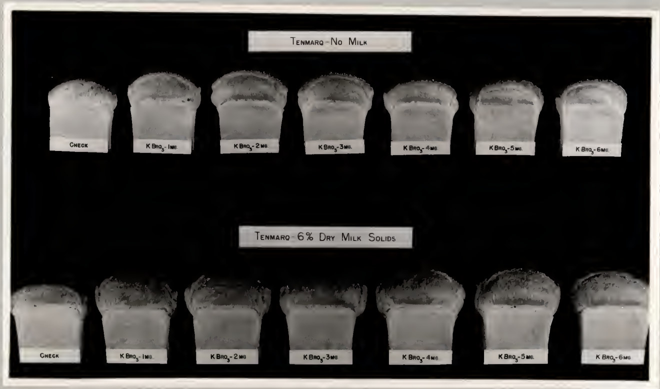


Fig. 6. The effect of dry milk solids in relation to increments of potassium bromate on loaf exterior. Tenmarq wheat flour.

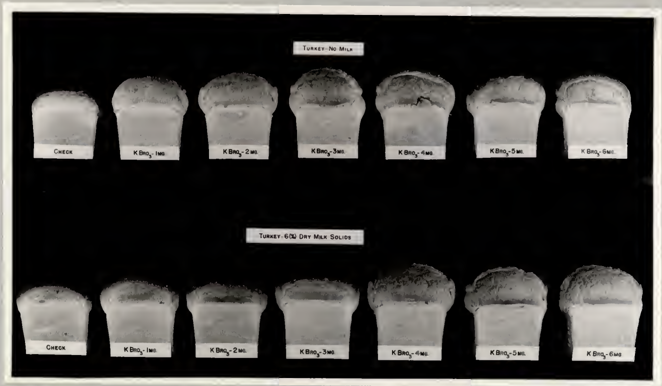


Fig. 7. The effect of dry milk solids in relation to increments of potassium bromate on loaf exterior. Turkey wheat flour.

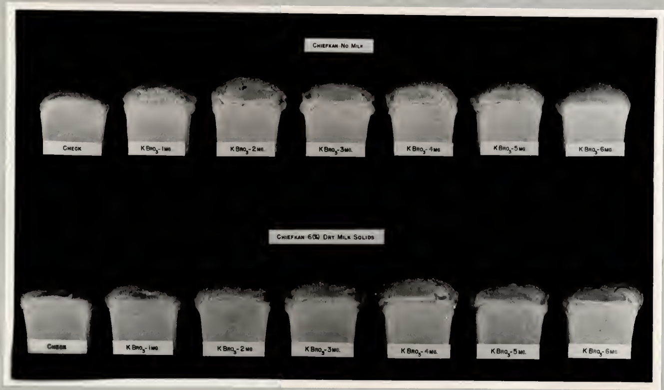


Fig. 8. The effect of dry milk solids in relation to increments of potassium bromate on loaf exterior. Chiefkan wheat flour.

The data clearly show, with but three exceptions (Turkey, Beta Chlora 1.13 oz. and 2.25 oz., and potassium bromate 2 mg.), that the presence of 6 percent dry milk solids increases the loaf volume over that obtained when no dry milk solids are included. Tolerance to potassium bromate was obtained through the use of dry milk solids suggesting that dry milk solids act as a buffering agent. This effect was not as noticeable as that shown by Ofelt and Larmour (1940). Table 5, Plate IV and Fig. 8 show this buffering effect was most noticeable in Chiefkan. Dry milk solids increased the bromate requirement needed for optimum loaf volume and loaf characteristics in all three varieties as given in Table 2. The crust color, break and shred, and general appearance of the loaf were also greatly improved through the use of dry milk solids. This is best shown by the photographs. The grain and texture were also improved. It was found easier to check duplicates when the formula included dry milk solids than when it did not, giving evidence that a more uniform loaf could be obtained when dry milk solids was included in the baking formula. These results were quite similar to the findings of Ofelt and Larmour (1940).

That the bread was gradually improved by the additions of Agene and Novadelox was indicated by a gradual increase in loaf volume and baking score with increasing amounts of these bleaches. The use of Beta Chlora gave less regular results than the other two bleaches. This was more pronounced with dry milk solids than without it. There was evidently less buffering effect from dry milk solids when Beta Chlora was used as a bleaching agent than when potassium bromate was used.

Although not commercially practicable four times the average commercial bleach was employed to find if such treatment would cause the flour to break down as it does with an excess amount of potassium bromate. According to the literature on flour bleaching, all bleaching agents with the possible exception of Novadelox are thought to lower the pH of the dough. This is evidently due to the acidic properties of the bleaching agents and the end products formed. Beta Chlora gave the only evidence of over bleaching, this occurring with the intermediate treatments. The fact that more chlorine, which has definite acidic properties, was used in making a normal treatment of Beta Chlora than a four-normal treatment of Agene probably accounts for the difference in the behavior of the two bleaches. Apparently Beta Chlora in some instances produced a condition which was more adverse to dough development than from the other bleaches studied. The doughs containing flour bleached with very high amounts of

Beta Chlora produced bread with improved loaf volumes. The pH as a result of this amount of bleach may have been beneficial. Although these conclusions were based on data differing within experimental error in some cases, the trend was so general that it seemed worthy of mention.

Beta Chlora gave the least improvement in the bread while Novadelox generally considered as a color improver was on a par with Agene. Novadelox, which in commercial practice is added usually in conjunction with one of the gaseous bleaches for the purpose of improving the flour color gave loaf improvement comparable to Agene and better than Beta Chlora. This observation was of interest from the standpoint that possibly Novadelox has promise of becoming a bread improver.

It was thought that possibly the loaf volume increase from Novadelox was due to the filler acting as a yeast food. The flours after eight months of storage at 40°to 42°F. were baked in the same manner as four months previously at which time improvement in loaf volume was noticeable. Six percent dry milk solids were used in these bakes, results for which are presented in Table 6.

Some definite change evidently took place in the flour after eight months of storage. The general benefit in loaf volume found after four month's storage, was lacking after

Table 6. The effect of Novadelox and storage upon baking quality of three flours.

Flour	Novadelox oz. per bbl.	Four month's storage: Loaf volume in cc.	Four month's storage: Total baking score	Eight month's storage: Loaf volume in cc.	Eight month's storage: Total baking score
Tenmarq	0	736	92.7	775	102.7
	0.40	747	97.5	796	105.6
	0.80	757	98.8	798	106.8
	1.60	791	104.3	814	108.4
Turkey	0	638	68.9	705	86.5
	0.40	655	77.8	701	88.8
	0.80	663	80.6	704	90.8
	1.60	673	85.1	705	90.2
Chiefkan	0	606	66.4	644	70.7
	.40	624	75.7	642	72.5
	.80	639	78.3	645	74.2
	1.60	645	78.7	645	74.2

eight months, with the possible exception of Tenmarq. The loaf volumes from the older flour tended to run at a higher level with less spread between extreme treatments and compared with the highest loaf volume of any treatment of the younger flour. The total baking score was increased with increased amounts of Novadelox as a result of improved crumb color, grain and texture. The problem of testing the effect of Novadelox filler has been outlined more completely and is scheduled for next year when green flour can be used in all cases.

These findings were similar to those of Ferrari and Bailey (1929) who stated that the flours bleached with the larger amounts of Novadelox did not maintain their advantage over smaller amounts after a comparatively long time.

The doughs became tighter as the amount of potassium bromate or bleaching agent used was increased, giving evidence that these treatments increased the water absorption. The use of optimum amounts of potassium bromate produced larger and better bread than did any from bleached flours. As a result it appears, therefore, that "oxidation" by bleaching and "oxidation" by potassium bromate may be of a different type and the terms should not be used synonymously.

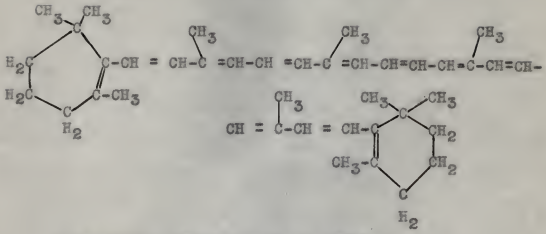
This series of flours provided an excellent basis for variety comparisons. It can be readily seen that bleached Tenmarq without the benefit of dry milk solids was superior to Chiefkan with or without dry milk solids. This statement also held true when the optimum amount of potassium bromate was used. The superior gluten quality of Tenmarq as compared to Chiefkan apparently enables it to respond more as a result of adding bromate or dry milk solids in spite of the fact that this Chiefkan sample was higher in protein than the Tenmarq. A high quality gluten variety like Tenmarq not only makes better bread production possible but responds more favorably to dry milk solids.

Turkey definitely had a high requirement for potassium bromate while Tenmarq did not. This was substantiated by the spread of optimum levels of bromate in milk-free and milk-containing doughs as shown in Table 2. Turkey had a spread of from 2 to 6 mg. (4 mg.) while Chiefkan and Tenmarq had a spread of 2 to 4 mg. (2 mg.). Turkey did not respond to bleaching action relatively as much as did Tenmarq. Potassium bromate seemed better suited to give a type of action required by Turkey while Tenmarq, although it gave better dough development with potassium bromate than bleach, showed greater response to bleaching both adversely and beneficially than Turkey. Tenmarq apparently had some gluten characteristics which allowed it to develop to a greater extent than Turkey when treated with bleaching agents. Tenmarq also definitely displayed the greatest improvement upon the addition of dry milk solids. Chiefkan with dry milk solids had a wider tolerance range with potassium bromate than any of the varieties investigated. The Tenmarq and Turkey total bread scores at optimum bromate levels with dry milk solids were similar and differed only two points.

Carotene determinations (Tables 3, 4 and 5) showed that carotene content varied inversely as the amount of bleach. These determinations were made to insure the accuracy of the bleaching apparatus (Plate I). Based upon the carotene content of the flours the bleaching apparatus indicated that it was very capable of measuring gaseous bleaches for one-pound samples of flour.

The yellow coloring matter found in wheat flour is thought to come principally from B-carotene. This pigment consists wholly or chiefly of a long acyclic chain of carbon atoms united in an uninterrupted sequence of conjugated double bonds, which system of conjugations functions as the chromophore.

The formula of B-carotene is as follows:



B-Carotene (Peterson _et al_ 1939).

The chromophore portion of B-carotene is composed of a series of ethylene groups (-HC=CH-) which form addition compounds with bromine, chlorine,and iodine. It is an elementary principle of organic chemistry that when ethylene is brought in contact with certain elements or compounds, it forms new compounds by adding atoms or groups of atoms. In this process two univalent atoms or groups of atoms are added to the hydrocarbon and a saturated compound is formed.

The color decreases in intensity as the double bonds of B-carotene split and form addition compounds with such active compounds as are introduced when bleaching agents are applied. Any substitution into the hydrogens of the ionone ring at both extremities of the molecules has no marked effect on the color of the molecule.

Beta Chlora removed less carotene in all varieties than Agene or Novadelox, the latter two being quite comparaeble in their results. The effect of bleaching agents upon carotene was different from that of potassium bromate as evidenced by the increased whiteness in crumb color of bread from bleached flours. Bread made from unbleached flour but with added potassium bromate possessed a yellower crumb than did the bread made from the bleached flours. This observation further differentiates between bleaching and bromate action and indicates the terms should not be used synonymously.

Variety apparently had some effect on the carotene content of the samples. Tenmarq (Table 3) in the unbleached form had the least followed by Chiefkan (Table 5) while the greatest amount was found in Turkey (Table 4). However, carotene content decreased relatively the same for all varieties as the amount of bleach increased. As the higher treatments were reached there was a tendency for the carotene figure to decrease less rapidly. With average normal treatments flour and crumb colors were of such a nature that the effect of higher treatments was not easily noticeable.

Bread doughs are highly complex colloidal systems of a very involved nature. The addition of dry milk solids, another colloidal complex, makes the dough-system even more complex. Any attempts to explain the action of dry milk solids in the bread dough must therefore be entirely theoretical. All that can be hoped for in an investigation of this type is to discover characteristic behaviors which will lead to a more sound foundation of knowledge in order to further study this problem. It is beyond the ability of the writer and the scope of this investigation to advance a theory pertaining to the action of dry milk solids in bread doughs, but the writer does wish to point out some of the effects which result from such additions.

It is believed that dry milk solids have a "buffering effect" as shown in this investigation and more extensively by Ofelt and Larmour (1940). This effect was given the name "buffering" because potassium bromate has an influence on the oxidation-reduction potential. Dry milk solids apparently acts as a shock absorber. This stabilizing action was not as evident in overbleaching with Beta Chlora perhaps because overbleaching is more concerned with pH change while bromating is more closely related to oxidation-reduction. If, on the other hand, both actions take the form of an oxidizing reaction there is the possibility that they attack different constituents of the bread dough.

It was evident that there were differences upon flour doughs between treatment with bleaching agents and treatment with potassium bromate. Bleaching agents had a great effect upon the coloring matter (carotene) of flour producing a colorless derivative. Some effect upon the gluten and baking properties was also evident. As a result of bleaching treatment the crumb color was whiter, and the volume, grain, and texture were noticeably improved. Potassium bromate, on the other hand, had no effect whatsoever upon the coloring matter. Potassium bromate, however, increased the loaf volume, and improved the grain and texture to a much greater extent than did the bleaching agents. It was thought from this that potassium bromate had effect wholly on the gluten proteins.

Whatever course of explanation is followed as to the effect of dry milk solids in the bread dough, a point remains which is of great practical importance to the miller and baker. When dry milk solids are used, the baker may accidentally use excessive amounts of bromate with an unknown flour without endangering markedly the quality of the finished loaf.

SUMMARY AND CONCLUSIONS

1. A study was made of the effects of commercial bleaching agents and of potassium bromate upon the color

and baking characteristics of flours from Tenmarq, Turkey, and Chiefkan wheats. In addition the effect of dry milk solids was studied after the flours were given varied bleaching treatments as well as varied quantities of potassium bromate.

2. Dry milk solids, when included in the baking formula, was used at the 6 percent level. The flours were baked with amounts of potassium bromate ranging from zero to 7 mg. per 100 g. of flour. Agene, Beta Chlora, and Novadelox were the commercial bleaches used in amounts ranging from zero to four times the normal treatment.

3. The results obtained clearly indicated that the presence of 6 percent dry milk solids confers a certain degree of tolerance toward potassium bromate, increases the loaf volume, and improves the grain, texture, and crust color.

4. The bread was gradually improved by the addition of increasing amounts of Agene and Novadelox. Beta Chlora at intermediate treatments gave small loaf volumes with a trend toward increased loaf volumes with light and heavy treatments.

5. The carotene content of the flour varied inversely to the amount of bleaching agent used.

6. The effect of bleaching agents and the oxidizing effect of potassium bromate should not be considered the same because in no case was the loaf volume or total baking score from bleached flours comparable to that obtained with potassium bromate at the optimum level. Bleaching whitened the crumb color while potassium bromate did not.

7. Chiefkan proved inferior to Tenmarq in baking quality. Turkey gave the most response to potassium bromate. Tenmarq tended to have the least carotene content and responded the most to bleaching treatment and to the addition of dry milk solids.

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