THE EFFECT OF BROMATE ON FLOUR DOUGHS - [illegible]

THE EFFECT OF BROMATE ON FLOUR DOUGHS - DEMPSTER

THE EFFECT OF POTASSIUM BROMATE ON PHYSICAL PROPERTIES AND STRUCTURE OF FLOUR DOUGHS

A Thesis

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by

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INTRODUCTION

There are many factors which cause a variation in the baking strength of wheat flour, i.e. the capacity of a flour to yield large light, fine-textured loaves of bread. Above all, the quality of the wheat from which the flour is milled is of prime importance. It is known, however, that flour, when freshly-milled, does not exhibit its maximum potentialities in baking strength; and that the baking strength gradually increases to a maximum if the flour is stored for a period of several weeks. This increase in baking strength is reflected in a gradual increase in loaf volume if flour samples are baked, according to a rigorously standardized procedure, at intervals during the storage period. In general, the larger a loaf of bread obtained from a given weight of flour, the less dense will be that loaf and the finer will be the texture of its crumb. Since the North American consumer prefers a fine-textured loaf of bread, it is important to be able to realize, in practice, the maximum potentialities of any particular flour.

Fortunately, it is not necessary for the flour miller or the baker to have facilities for storing large amounts of flour over a period of several weeks to promote its maturation, since the addition of minute amounts of certain chemical reagents to freshly-milled flour or to doughs mixed from freshly-milled flour has a pronounced effect in simulating the effect of aging. Such reagents may promote a large increase in loaf volume together with a definite refinement or development of texture. The loaf volumes obtained by baking doughs mixed from freshly-milled, untreated flour and containing small amounts of such reagents closely parallels the volumes obtained by baking doughs prepared from the same flour when fully matured by aging. Substances which are used to produce these beneficial effects in dough and bread prepared from freshly-milled flour are known as "improvers".

The knowledge that freshly-milled flour can, with the help of improvers, be used to produce satisfactory light, palatable loaves of bread is obviously of considerable economic importance, and widespread use is made of improvers in both the milling and baking industries. Largely because of their importance, a number of workers in the field of Cereal Chemistry have attempted to investigate the chemistry involved in the changes produced in dough and bread properties by minute amounts of these reagents. Much has been written on this subject, but a good deal of this information is empirical and some of it controversial. The present study was undertaken in an attempt to resolve, in some degree, this confusion and to elucidate more clearly, if possible, the chemistry underlying the changes which occur with time, in the physical properties of flour dough containing minute amounts of improvers, specifically potassium bromate.

Ever increasing importance is being attached, today, to the study of high polymers. One of the largest groups of polymers is that of the naturally occurring substances among which are included the proteins. Now, protein is an important constituent of wheat and flour, and plays an important role in determining the physical behavior of dough. It was thought, therefore, that the application of physical chemical methods, such as those used in high polymer studies, to an investigation of changes produced in dough properties by minute amounts of improvers might prove useful in studying the chemistry involved.

Consideration of two well-known properties of flour dough and of gluten, the protein of wheat and flour which can be recovered from dough by washing, gives rise to an interesting hypothesis of dough and gluten structure. These properties lead to the postulate that dough and gluten are high polymeric materials in which the behavior is determined by an internal cross-linked structure.

The particular properties which suggest that the physical behavior of dough and gluten is determined by a network structure in the material are:

(1) flour dough and gluten exhibit so-called rubberlike elasticity,

(2) gluten, which is largely protein exhibits a very definite limited swelling in water and does not imbibe water indefinitely, when placed in water, to become dispersed in the manner of proteins generally.

Meyer (54) has stated that if a substance swells when placed in certain liquids, without passing into solution, it may be concluded that the material in question is a high polymer. Further, when limited swelling occurs, it is to be concluded that some sort of three-dimensional continuity, by means of cross-links, exists in the material.

Natural and synthetic materials possessing rubberlike elasticity have been termed elastomers. Recent studies of elastomers in general have established certain basic structural concepts. In so far as flour dough and gluten, which exhibit rubberlike behavior, are elastomers, these concepts must apply. The following conditions have been postulated as necessary in a material exhibiting rubberlike behavior, (76):

(1) presence of long chain molecules which are flexible by virtue of free rotation about bond links. These molecules exhibit a constant sinuous motion as a result of kinetic energy associated with the segments,

(2) a few points of cross-linkage between the long chain molecules giving rise to a three-dimensional or network structure,

(3) weak secondary forces of interaction between the long chain molecules.

The network structure is essentially a dynamic structure. In an unstretched state, the network chains, i.e. the long polymer molecular segments between the cross-links, assume randomly coiled configurations. Some of the long chain molecular segments will be folded up at a given instant, others will be fully extended, and there will be a statistical distribution between these two extremes. The majority of the molecular segments will have a Most Probable Length intermediate between the two extremes. In a stretched state, the network chains are forcibly uncoiled and displaced from their most probable length. When the deforming force is removed, the kinetic motion of the molecular segments tends to cause the network chains to return to their most probable length. This is considered to be the source of rubberlike elasticity.

A number of workers have developed the network-statistical theory of rubberlike elasticity (18, 38, 47, 75, 77). An "equation of state" for flexible polymer networks, expressing the force of retraction in a stretched polymer as a function of temperature, elongation, and network structure, may be written:

$$\tau = \frac{\nu}{V} RT \left[\frac{l}{l_o} - \frac{l_o^2}{l^2} \right] \qquad \text{(i)}$$

τ = retractive force per unit initial cross-sectional area

R = gas constant

T = absolute temperature

l = stretched polymer length

l_o = unstretched polymer length

$\frac{\nu}{V}$ = a proportionality constant characteristic of the polymer sample and dependent on structure, which has been called the network activity.

A significant feature of equation (i) is the predicted dependence of the retractive force on the network structure as embodied in the factor $\frac{\nu}{V}$. The elastic theories do not, however, agree on the exact dependence of the proportionality constant $\frac{\nu}{V}$ on network structure. In several of the theories, this quantity is proportional to the number of "chains" per unit volume where the "chain" is defined as the part of a molecule extending from one cross-linkage to the next.

For an ideal network formed from indefinitely long molecules, the number of chains is identical with the number of cross-linked monomer units or equal to twice the number of cross-linkages. If a fraction ρ of the structural units is involved in cross-linkages, the concentration of chains (moles per cubic centimeter) is $\frac{d}{M_o}\rho$ and the theoretical relation between network activity and degree of cross-linking is given by:

$$\frac{\nu}{V} = g \frac{d}{M_0} \rho \tag{ii}$$

d = density of the polymer (grams per cubic centimeter)

M_0 = molecular weight of the structural unit.

The proportionality constant, g, is unity in the theories developed by Wall (77), Treloar (75), and Flory and Rehner (18). Kuhn (47) believes g should have a value of 7/3 while James and Guth (39) conclude that g should be above 1/2.

Flory (15, 16) has modified equation (ii) as a result of considering that each primary molecule will give rise to two inactive terminal ends in the network structure. This leads to the consideration of an effective degree of cross-linking and ρ of equation (ii) is modified by the subtraction of a correction factor.

$$\frac{\nu}{V} = g \frac{d}{M_0} \left[\rho - \frac{2}{\overline{\overline{y}}_n} \right] \tag{iii}$$

Thus, this equation takes into account the molecular weight of the polymer before cross-linking since $\overline{y}_n$ is the number average degree of polymerization prior to cross-linking.

Polymers possessing a network structure exhibit a limited swelling when placed in suitable liquids. A thermodynamic treatment of the swelling phenomenon (19) relates equilibrium swelling volume and network activity $\frac{\nu}{V}$:

$$\frac{\nu}{V} = \frac{\ln (1 - v_2) + v_2 + \mu_g v_2^{2}}{- V_1 \ v_2^{1/3}} \tag{iiii}$$

v_2 = the reciprocal of the swelling volume (where the swelling volume is the ratio of the volumes of the swollen and dried gel),

μ_g = solvent-polymer interaction coefficient,

V_1 = molar volume of the solvent.

When a high degree of swelling takes place (i.e. v_2 small), equation (iiii) reduces to the approximate expression

$$\frac{\nu}{V} \doteq \frac{(1 - 2\mu_g)\, v_2^{5/3}}{2V_1} \qquad \text{(v)}$$

The relation between retractive force and equilibrium swelling volume is derived by combining equations (i) and (v), thus:

$$\tau = \frac{RT\left[\frac{1}{l_0} - \frac{l_0^2}{l^2}\right](1 - 2\mu_g)\, v_2^{5/3}}{2\,V_1} \qquad \text{(vi)}$$

The theory then predicts that the retractive force at a given elongation should be inversely proportional to the 5/3 power of the swelling volume.

Experimental investigations on the dependence of the retractive force of stretched polymers on the degree of cross-linking are limited. Flory has shown that butyl rubber swollen in cyclohexane conforms to equation (vi) (16). Flory, Rabjohn, and Shaffer (17) observed the dependence of retractive force on the degree of cross-linking for natural rubber vulcanizates and for GR-S polymers. Their theoretical considerations predicted a linear relation between these variables. Experimentally, deviations were found to occur. The change in retractive force of rubber vulcanizates with degree of cross-linking was less than predicted, τ being higher than predicted for low degrees of cross-linking, while the reverse was true at high degrees. Results obtained on GR-S polymers agreed with theory somewhat better, but deviations from linearity were still observed. The results did demonstrate a progressive increase in the force of retraction at a fixed elongation with an increase in the fraction ρ of the structural units which are cross-linked.

Bardwell and Winkler also investigated the effect of network structure on the elastic properties of GR-S polymers (9, 10, 11). Vulcanization of these synthetic rubber samples was accomplished by treating GR-S latex with potassium persulfate, and the degree of cross-linking was calculated from the gel-to-sol ratio. The rate of cross-linking was found to be proportional to the concentration of persulfate. The proportionality between network activity and the effective degree of cross-linking predicted by statistical considerations of rubber elasticity was verified for low degrees of cross-linking.

These studies on natural rubber vulcanizates and GR-S polymers show that the retractive force of stretched polymers is directly related to the degree of cross-linking. Deviations from theoretical predictions are observed but these are believed largely due to oversimplifications in the statistical treatment of the network structure.

Flour dough and gluten appear to satisfy some of the elastomeric requirements. The requisite long chain molecules are to be found in the flexible long chain polypeptide protein molecules. These flexible molecules are capable of assuming a variety of lengths in accordance with kinetic theory and possess a most probable shape which is rodlike. Gluten exhibits a limited swelling and an insolubility in water. The occurrence of a limited swelling suggests that the individual protein chains are held together by definite chemical forces in some sort of three-dimensional network. The segments of the long chains, between the postulated cross-links, possess the property of hydration and consequent swelling possibly because of the presence in the chains of hydrophilic groups. The swelling is limited, however, by the number of these groups and by the chemical forces of the network.

Studies on proteins in general have demonstrated that the polypeptide protein chain is made up of known amino acids united by a primary valence bond called the peptide linkage, - CO - NH - . This is a link in one direction only since the proteins are long chain molecules.

The second elastomeric requirement is that there be cross-linkages between the long chain molecules forming a loose three-dimensional network. Spencer, discussing the phenomenon of rubberlike elasticity (64), states that the linkage points in a network structure may be strong chemical primary bonds, chemical bonds capable of breaking under a stress and subsequently reforming, or even points of strong secondary forces.

Little actual experimental evidence is available as to the possible types of cross-links involved in dough and gluten structure. Some workers have assumed that the disulfide linkage is involved (2, 32, 67). Hlynka (36) has suggested the possibility of cross-linkage formation in dough by a reaction between carbonyl groups of reducing carbohydrates and amine, amide, or guanidyl groups of proteins. Nevertheless, if it be assumed that cross-linkages between protein chains are responsible for elasticity in dough, then changes in elasticity of dough result from changes in the number of cross-linkages between the main chains.

Since there appears to be good reason for regarding the structure of flour dough as comparable with a polymer network, it seems reasonable to seek a relation between the properties of the network and the physical properties of the dough. Improvers are known to influence the baking strength of flour. If baking strength and the network properties of dough are intimately related, then it is to be inferred that improvers influence the polymer network. A study of the chemistry of the improving action of potassium bromate in flour doughs therefore resolves itself into a study of the effect of bromate on such measurable properties of dough as may be expected to depend upon the existence and properties of a network structure.

The literature contains a multitude of papers on the use and function of the improvers utilized by flour millers and bakers to enhance one or more qualities of flour, dough, and bread. Substances which have been used as aids in improving the quality of flour, dough, or bread are many and varied. However, in this work, attention has been confined largely to one of these reagents, namely potassium bromate, and its effects on the properties and structure of dough. Some other experiments have been made in which the effects of oxygen and the effects of the cupric ion on physical dough properties were investigated. These relatively few experiments were made in the hope that they might shed additional light on the main topic.

With a view to subsequent discussion of the main aspects of the present investigation, it is necessary to review previous studies of the effects of bromate on dough and bread properties. This review falls conveniently into three parts. First, an outline will be given of the general methods which have been utilized in investigations of the changes produced in dough and bread properties by added reagents. Second, the investigations dealing only with the gross effects of added reagents on dough and bread properties, i.e. the phenomenology of the reactions, will be presented. Finally, consideration will be given to the investigations and discussions pertaining to the various theories already proposed to explain the effects of bromate in dough and bread. It will become apparent that, although the reaction of bromate in dough has been the subject of a number of investigations, it is still a very controversial issue. There is little agreement between the various workers concerning the mechanism whereby the changes occur in dough properties as a result of incorporation of bromate.

Investigations of the physical properties of wheat flour doughs have been made for many years. Early workers were impressed with the fact that dough had certain properties in common with both solids and liquids. It resembles a solid in that it exhibits elastic properties, but it resembles a liquid in that it will flow to some extent. Generally, when the behavior of dough is observed, both of these factors are found to be involved. When a dough is subjected to a stress, both elastic and viscous deformations are observed. The former are completely recoverable, while the latter are non-recoverable when the stress is removed.

Attempts to measure the physical properties of flour doughs were reported in the literature at quite an early date (4). Over a period of years a number of mechanical dough-testing instruments have been designed, capable of measuring a complex mixture of properties of dough. Such machines have yielded little knowledge of the actual structure of flour dough, largely owing to the difficulty of definitely identifying the physical, or more strictly, mechanical dough properties, as revealed by the particular machine, with the fundamental physical properties of the material such as elasticity or viscosity. Nevertheless, mechanical dough-testing instruments have often been used in studies of the behavior of flour dough under differing conditions. A vast amount of useful, though fundamentally empirical, information has been accumulated in this way.

Mechanical dough-testing instruments may be classified into two general groups. These are (a) recording dough mixers, and (b) instruments which are concerned with measurements of the extensibility of doughs or of the resistance offered by them to extension. A comprehensive review of such instruments has been given by Bailey (4).

The principle of the recording dough mixer seems due to Hogarth. His instrument had a small dough mixer provided with a dynamometer attached to the drive, and a stylus recorded on a chart the force applied at all times during a prolonged mixing period. The modern Farinograph is based on this same principle. This instrument, however, has a temperature-controlled mixing chamber. The curves or farinograms show that the force applied in the initial stages of mixing rises more or less rapidly to a maximum where it remains virtually constant for varying periods of time depending on the properties of the particular sample. The force then gradually recedes.

One of the major applications of this instrument is to measure the relative plasticity of dough samples. The maximum height to which the curve rises on initial mixing is regarded as an index of the absorption of the flour, i.e. the proportion of water added to flour necessary to produce optimum plasticity in the dough. Two other dough characteristics may be determined from farinograms. One of these is the time required for dough formation or the optimum mixing time, the other is the mixing tolerance or the amount of mixing in excess of the optimum that a dough will tolerate before its properties begin to deteriorate. The farinograph can be used to indicate the effect of certain reagents on dough properties by virtue of changes produced in these "machine dough characteristics".

Schofield and Scott Blair (61) studied the behavior of flour dough using an instrument called a mercury trough extensimeter. In this extensimeter, a cylindrical dough sample which had been extruded from a specially-designed dough "gun" was floated on a pool of mercury. Graduated scales, which could be viewed through a low-powered microscope, were attached to either end of the dough. One end of the dough sample was attached to a calibrated spring and the other end to a winch by means of which stresses could be applied to the dough. This instrument permitted study of dough properties at either constant sample extension, in which case the stress decays with time, or at constant stress, in which case deformation increases.

Another widely-used dough-testing instrument is the Brabender Extensograph (4). This instrument is designed to stretch a cylinder of dough, of known dimensions, at a constant rate into an elongated U-shape until the sample breaks. An automatic recording device traces out a curve indicating the force required to extend the dough as a function of the amount of extension. These load-extension curves, or extensograms as they are called, resemble skewed segments of circles. The exact shape of the curve depends upon the interaction of the elastic and viscous properties of a given dough.

The physical or mechanical properties of flour doughs that are indicated by the extensograph are markedly influenced by the presence in dough of potassium bromate. As a result, this instrument has been quite widely used in studies of the effect of bromate on dough properties. Unfortunately, however, the extensograms are to a large extent empirical since they can not be interpreted in terms of fundamental properties such as elasticity or viscosity. To date, extensograph studies of the changes produced in dough properties by the addition of bromate have yielded little fundamental knowledge of the reactions involved.

These are but a few of the dough-testing machines which have been designed to measure one or more of the physical properties of flour dough. These machines, together with certain experimental procedures such as the differential baking test (79), have been frequently used to assess the effects produced in dough and bread properties by the addition of potassium bromate.

The use of potassium bromate as an agent in bread-making appears to have been first reported by Kohman, Hoffman, and Godfrey (44, 78) in 1915 in British and United States patents. Bromate was added to the other ingredients of a dough, before fermentation, either by itself or as one component of a mixture of NH_4Cl, $CaSO_4$, and $KBrO_3$. Kohman and co-workers, in a subsequent paper (45), described their investigations leading up to these patent applications. They had studied the factors involved in producing bread of uniform quality in different locations under different conditions. They recommended the use of minute amounts of ammonium salts to stimulate the yeast fermentation, and the addition of calcium salts to diminish differences in bread quality from one locale to another due to variations in mineral content of the water used in making the dough. The addition of bromate, it was stated, did not affect the yeast but rather acted upon the dough itself imparting very desirable properties to it.

The effect of an exceedingly small amount of potassium bromate upon the dough was classed as an aging, or maturing, effect. The beneficial action of bromate in dough was characterized by an increase in the volume of the resulting bread loaf and by an improvement in bread texture as compared with bread made from untreated doughs. It was reported that there was an optimum concentration for bromate addition which, if exceeded, produced a stiff or "bucky" dough and resulted in diminution of loaf volume to values much less than that of even an unbromated loaf. The effects of bromate in dough were attributed to the oxidizing power of the salt since oxygen, incorporated into a dough, had a similar action although to a lesser degree. The observations of Kohman and co-workers, concerning the effect of the bromate-containing baking ingredient on bread properties, were confirmed by Herman and Hart (35).

Blish and Sandstedt (12) reported that the addition of 1 mgm. of potassium bromate, in solution at the time of mixing the dough, to a loaf prepared from 100 gm. flour produced an extraordinary increase in loaf volume and a decided refinement or development in crumb texture. The degree of stimulation was found to be proportional to the protein content of the flour. Harris (34), studying the effect upon loaf volume of adding successive increments of bromate to doughs from flours of different protein contents, found that the higher protein flours reacted more vigorously to the higher concentrations of bromate. The improvement which accompanies the incorporation of bromate into dough apparently does not alter the hydrogen-ion concentration in the resulting bread (33).

A number of workers have investigated the relation between the protein content of wheat and the volume of the bread loaf produced from the resulting flour with results that tended to suggest a linear relation between these factors. Deviations from linearity became quite pronounced both at low and high protein levels. Larmour (48) found that when flours were baked using bromate in the dough formula the linearity of the protein content-loaf volume relation was extended over a much larger protein content range. Geddes and Larmour (28) reported that the loaf volumes obtained by baking doughs from freshly-milled flours, and containing small amounts of bromate, closely paralleled the volumes obtained by baking doughs, without bromate, prepared from the same flour when fully matured by natural aging.

Larmour and Brockington (49) discussed gas production and gas retention, two very important factors in determining bread properties. They reported that potassium bromate had a distinct effect only on the gas retention property of dough. Bromate seemed to increase retention in strong flours and to decrease retention in weak flours. One of the effects of incorporating bromate into dough has been reported to be an increase in the gas pressure required to expand the dough, suggesting that the modulus of elasticity of the dough had been raised (6).

The addition of wheat germ to flour has been reported to cause deterioration of dough and bread properties, but the addition of bromate, or heat treatment of the fresh wheat germ before addition to the flour, reduced the detrimental effect (28). The deleterious effect of germ on bread properties decreased as the germ aged, and coincidentally the improvement produced by bromate was found to decrease as aging progressed. These effects were attributed to changes in the phosphatides present in the flour.

Many workers have used one or more of the various types of recording dough mixers in their studies of the effects of added reagents on dough properties. Since such machines record the force required at any instant to drive the mixing pins through the dough, they apparently measure the relative viscosities of doughs. The addition of certain reagents to doughs being tested in these machines may produce marked changes in the dough properties and this, of course, shows up in the resulting curves. By studies with such an instrument, the deleterious effect of wheat germ, added to flour dough, has been shown not to result primarily from the lipid components. The use of water extracts of germ in testing flour doughs in the farinograph illustrated that the harmful component was water soluble (68, 69), and this was verified by baking tests. It was later demonstrated that glutathione was the harmful germ constituent (65). The sulfhydryl compound, cysteine, was also found to have a deleterious effect on dough properties as measured by the farinograph, but cysteine-treated doughs produced normal bread loaves.

Indications are that the recording dough mixer type of instrument fails to reveal the effects of bromate addition on dough properties. This observation has been noted in studies with the farinograph (55) and with the mixograph (71). When the effect of the proteinases pepsin, trypsin, and papain on dough characteristics were measured by the mixograph, it was not possible to demonstrate that bromate added to dough had any inhibiting effect on the above proteinases.

Swanson (71) and Swanson and Andrews (72, 73) explained the results of continuous mixing studies on the basis of the following concept of protein structure in dough. The protein, or gluten, was envisaged as continuous in dough and bread to form a three-dimensional fibrillar or brush heap structure. During the initial mixing, which is characterized by an upward sweep of the mixograph curve, water is brought into contact with and absorbed by the starch granules and the protein of the flour. Gluten strands tend to become oriented into a more or less parallel pattern as mixing progresses. This continually developing arrangement increases the resistance offered to the movement of the pins of the mixer through the dough. The maximum resistance to the movement of the pins occurs when there is the greatest parallel arrangement of the gluten strands in the dough and before the strands begin to disintegrate. Disintegration of the gluten strands is probably the cause of the decrease in resistance offered to the mixer pins when the mixograph curve shows a decline.

The concept that the strands of gluten become oriented into a more or less parallel pattern as mixing progresses is somewhat suggestive of the phenomenon of Rheopexy. This is the name given to the process of quick solidification of certain thixotropic fluids which may be brought about by a slow, repeated regular movement. Freundlich and Juliusburger (21) observed that sols of gypsum powder of given concentrations, if left alone in tubes of 1 cm. diameter, solidified in about 40 minutes. However, if tubes of these same sols were rolled between the palms of the hands, solidification occurred in about 20 seconds. Acceleration of the process of solidification was due to the orienting effect of the work on the non-spherical sol particles.

The concept that the protein of dough forms a continuous network has been discussed in a more fundamental way by Schofield and Scott Blair (59, 60, 61, 62). These authors made a series of investigations on the fundamental physical properties of wheat flour doughs. They emphasized the fact that flour dough combined a high degree of plasticity with considerable elasticity and suggested that the concepts first put forth by J. C. Maxwell, concerning materials exhibiting both elastic and viscous behavior may be applied to doughs. According to Maxwell, the stress placed on a material exhibiting elastic and viscous properties decays with time according to the equation

$$S = S_0 e^{-t/\lambda} \qquad \text{(vii)}$$

S = the stress on the material at any time, t,

S_0 = the stress on the material at time $t = 0$,

λ = the time of relaxation of the material.

The reaction of a body to an applied strain is not instantaneous but in general requires a finite time which is characteristic of the molecular constitution of the material. This time, which is characteristic of the speed with which the molecules of the material will move to their new equilibrium positions when a stress is applied, is called the relaxation time. The relaxation time, λ, is related to the viscosity, η, and to the shear modulus, G, of the material by the equation

$$\lambda = \eta / G \qquad \text{(viii)}$$

Schofield and Scott Blair adapted these concepts to flour dough behavior by recognizing that the relaxation time, λ, was not a constant but varied as the applied stress.

Measurements were made of the elastic modulus and the viscosity of flour doughs and from these values the relaxation time, λ, was calculated. In this way, it was established that a relation existed between the physical properties of doughs and their bread-making qualities. For good bread-making, a dough of high relaxation time is desirable, i.e. a dough having a high viscosity and a low modulus. The pressure of the carbon dioxide formed in the dough by the fermentation process can then readily expand the dough but, because of the dough's high viscosity, the small bubbles of gas can not coalesce. This results in a dough which is fine-textured and light and these properties are reflected in the baked bread.

In some of their work, these authors studied dough properties using the mercury trough extensimeter. These studies led to the following hypothesis for the structure of flour dough. In dough, the gluten is pictured as forming an elastic network which dominates the mechanical behavior. This network does not establish itself immediately on mixing the dough but continues to build up for some time after cessation of the mixing operation. The branched protein chains of the gluten are joined together to form this network, of which the links were postulated to be of two types, one strong the other weaker. The electrostatic attractions between oppositely charged groups of atoms in neighboring molecules were shown to be a likely factor in determining the strength of the network. The time of relaxation was thought to be a characteristic of the connected structure as a whole, whereas the viscosity was governed by the plastic film by means of which the elastic elements were connected.

Bohn and Bailey (13) modified the mercury trough extensimeter by the inclusion of a direct reading stress balance. These authors observed the decay of stresses, with time, in doughs made from flours of high, medium, and low protein contents, which had been extended to 500 per cent of their original length, this deformation being maintained constant. The results of these experiments showed that the stresses were highest at all times for the high protein flours. A log.-log. plot of stress against time yielded a linear relation, the slope of which for each of the three flours was about the same.

The Brabender Extensograph, since its introduction into the field of physical dough-testing in 1936, has been widely used to study the physical properties of flour doughs. Munz and Brabender (55) reported that the effects on dough of added oxidizing agents such as potassium bromate, did not show up in tests involving the continuous mixing of doughs. However, the effects of such added oxidizing agents did become evident when the dough had been allowed to rest for a period of time before being subjected to test on the extensograph. Doughs were shown to exhibit quite different properties if tested when in an "excited" state due to immediate previous mixing, molding, or other manipulation and if tested after a considerable rest period.

In this type of dough test, a cylindrical dough sample is stretched at a constant rate into an elongated U-shape until the sample breaks. At the same time, the force required to extend the dough and the extent to which the dough has been extended are automatically recorded as load-extension curves. Munz and Brabender decided that the ratio of the maximum load to the maximum extension of the dough as read from the extensograms represented a convenient method of analysis of experimental results. Doughs tested soon after they had been molded into the required cylindrical shape exhibited a high value for this ratio, and this ratio was found to decrease with increasing time between molding and stretching. Experiments were made on doughs which had been allowed to stand for periods of two hours and four hours after mixing before being molded into the cylindrical shape for testing on the extensograph. The change in the load-extension ratio, with increasing time from molding to testing was also noted for these doughs. The change in this ratio with time after molding was termed "relaxation" but it was emphasized that this was not analogous to Maxwell's relaxation time as used by Scott Blair.

Changes in the dough properties, i.e. relaxation, as a function of rest period between molding and testing were followed for flour doughs containing 0 and 3 mgm. per cent potassium bromate, i.e. 3 mgm. bromate per 100 gm. flour. Untreated and bromate-treated doughs were allowed reaction times of 0, 2, and 4 hours between mixing the dough and molding it for test on the extensograph. It was observed in such tests that the relaxation proceeded more slowly in the bromate-treated doughs than it did in the untreated control doughs. In addition, for the bromate-treated doughs, the greater the reaction time between mixing and molding, the slower was the rate at which the relaxation proceeded.

These experiments illustrated that the extensograph properties of flour doughs changed considerably during the first 30 to 45 minutes after the doughs had been molded. However, for rest periods in excess of 45 minutes between molding and stretching on the extensograph, the dough properties changed very little. This observation was used as the basis for subsequent extensograph testing of doughs. Doughs were mixed, shaped or molded into the required test shape, and then rested for a period of 45 minutes before being stretched. Immediately after it had been stretched, the sample was reshaped, rested for a further period of 45 minutes and then stretched again. This cycle of operations was repeated over and over as long as it was desired to follow the changes in dough properties with time.

Using the above technique, Merritt and Bailey (52) investigated the effect of bromate addition on dough properties, as reflected in 45 minute extensograms. With increasing reaction time, the effect of bromate was to increase the capacity of the dough to support a load, and decrease the extent to which the dough could be stretched. Reducing agents produced a reverse effect with increasing reaction time, the load supported by the dough being gradually decreased and the extensibility increased. Bromate and sodium sulfite had a mutually compensating effect on extensograph dough properties when added simultaneously.

An attempt has recently been made to interpret the empirical extensograph test. Fisher, Aitken, and Anderson (14) discussed the load capacity and extensibility of doughs in terms of their probable relation to elastic and viscous deformations that occur when the dough is stretched. Both elastic and viscous properties were considered to be involved throughout most of the elongation. The elastic properties were considered to offer resistance to stretching until the extensogram showed that a maximum in this property had been attained, beyond which, to the break point, only viscous deformation was believed to be involved.

Flour doughs, on standing for a considerable time after being mixed, tend to undergo progressive softening. Halton (29) demonstrated that the softening exhibited by a flour dough was actually equivalent to an increase in the free water content of the dough. Some previous workers had tended to associate this progressive softening of doughs with proteolytic action. Using a specially-designed extrusion viscometer, it was demonstrated that the softening of untreated doughs with age was reflected in a fall of extrusion time and a similar trend was observed with increasing age of bromate-treated doughs. When bromated and non-bromated doughs of increasing age were subjected to extension tests, differences in behavior were noted (30). With unbromated doughs the progressive softening with time was evident in the extension tests, while with bromated doughs the progressive softening was not evident in this way. The effect of the bromate overshadowed the progressive softening and the extension tests revealed changes in dough properties due to the bromate.

Brief reference may be found in the literature concerning the effect of working a dough in relation to the changes produced by bromate in dough properties. Larmour and Brockington (49) reported that punching a dough, i.e. working a dough to remove carbon dioxide produced by fermentation, increased subsequent gas retention in both bromated and non-bromated doughs. It seemed, however, that a greater increase in gas retention was evident in bromated doughs after the doughs were given a second and a third punch. Baker and Mize (6) reported that bromate had little apparent effect on dough and bread properties in the absence of fermentation and mechanical action.

Since the discovery of the beneficial effects of adding small amounts of potassium bromate to dough, a number of theories have been advanced to explain the mechanism of its action. One of the earliest explanations advanced was that by Bailey in his monograph in 1925 (3). Bailey grouped bromate along with ammonium and calcium salts, phosphates and per-acids, as a class of flour improvers with yeast-nutritive value.

Kent-Jones (43) in 1927 discussed the action of flour improvers in terms of colloid chemistry. Flour, he pointed out, consists of a complex mixture of colloidal bodies, and flour strength was thus associated with the particular colloidal condition of certain flour ingredients. The increase of strength produced by traces of added reagents fitted in with the colloidal theory of flour. The influence of minute amounts of potassium bromate on dough, he argued, could not be due to an alteration of gross chemical quantities but must be a colloidal effect.

Geddes conducted baking tests on flour which had been heat-treated for varying times at different temperatures from which he inferred that the presence of phosphatides was deleterious to the baking strength of the flour.(26, 27). He reported that progressive improvement occurred in the baking quality of flour with increased time of heating at a constant temperature, or with increased temperature at constant time of heating. The improvement in baking quality of freshly-milled flour induced by heat was not comparable in magnitude with that produced by adding 0.001 per cent potassium bromate to unheated flour. However, heat-treatment induced the same general characteristics in the finished loaf. Geddes concluded that wheat germ was the constituent responsible for this behavior of flour. It was suggested, that the improvement in baking quality of flour produced by heat or by bromate resulted from the oxidation of some germ constituent, primarily the phosphatides.

Jørgensen conducted experiments on the autolysis of flour suspensions. He found, in comparative tests on bromated and non-bromated flour suspensions, that there was noticably less water-soluble nitrogen in the bromated samples. Similar results were found when potassium iodate was used, but not when potassium chlorate was used. Both bromate and iodate, it was pointed out, could function as flour improvers whereas chlorate could not. Both bromate and iodate were found to inhibit the proteolytic activity of papain and the proteases of wheat flour as judged by the ability of these enzyme preparations to liquefy gelatin to greater or less extent.

Jørgensen observed that glutathione, a substance possessing no proteolytic activity, virtually liquefied dough when added to it, and brought about an early breakdown of the mixed dough as determined by a farinogram, and had a damaging effect on loaf volume (41). Water extracts of yeast were found to affect farinograms and loaf volume in a similar manner. When bromate was added to dough simultaneously with glutathione or water extracts of yeast, the response to bromate was reported greater than when bromate alone was added to the dough.

Jørgensen (42) proposed the theory that the beneficial effects of bromate and other oxidizing agents on dough properties occurred because these substances inactivated the proteolytic enzymes of flour. He postulated that a certain optimum proteolytic activity was necessary in dough for the production of optimum bread qualities. The addition of minute quantities of oxidizing agents reduced proteolysis to near this optimum, but damage to bread properties resulted if proteolytic activity was reduced below this optimum level by incorporation of excess amounts of improvers.

Balls and Hale (8), in studies on the improving action of certain bleaching agents on flour, came to a similar conclusion independently of Jørgensen. Wheat flour, these authors reported, contained powerful but normally latent proteinases. In the presence of suitable activators such as glutathione, certain water-soluble yeast constituents, and cysteine, the proteinases which were thought to be enzymes of the papain type manifested themselves. The action of the proteinases of flour on dough changed the colloidal properties of the wheat proteins and this became evident in changes in the properties of the dough and gluten. The addition of an oxidizing agent to dough resulted in the oxidation of the proteinase activator, thus effecting a diminution of the proteolytic activity.

Support of the proteolytic inhibition theory has been offered by Zeigler (80, 81, 82), who published a series of papers concerning glutathione oxidation and the effects of both the reduced and the oxidized forms on dough properties. Bromate and iodate, both flour improvers, oxidized glutathione, while chlorate which is not a flour improver did not oxidize glutathione. The fact that bromate produced a gradual change in the properties of doughs was interpreted as due to its slow rate of oxidation of glutathione.

The proteolytic theory of Jørgensen and of Balls and Hale has received criticism by a number of workers. Read and Haas (58) reported that bromate, in the concentration used in the normal baking procedure, did not adversely affect the proteolytic power of flour proteinases when such were allowed to act on gelatin. However, when bromate was present in relatively large amounts with respect to the enzyme, it did repress the activity of papain. These workers pointed out that the ratio of bromate to flour employed by Jørgensen in his extraction tests greatly exceeded the ratio employed in the baking industry.

Sullivan, Howe, Schmalz, and Astleford (67) pointed out that the proteolytic theory was based, not on direct evidence, but largely on reasoning by analogy, e.g. bromate inhibits the gelatin-splitting ability of papain; HCN and SH compounds activate the enzyme; flour reacts in the same way and hence must contain a proteolytic enzyme of the papain type which exerts great influence. Shen and Geddes (63) recorded a similar argument. It was true, they said, that the addition of proteases to dough did give rise to considerable dough softening, but this, in itself, did not prove that proteolytic activity was of particular significance in the baking behavior of normal flours.

Ford and Maiden (20) carried out studies using the farinograph on doughs to which glutathione and papain, respectively, had been added. Glutathione had a direct and immediate softening action whereas papain, in addition to an immediate softening action, displayed a delayed softening effect. These authors believed that the effect of glutathione in dough was primarily associated with a direct action on the gluten proteins rather than with an activation of proteolytic enzymes. Balls and Hale (8) had earlier pointed out the possibility that such agents as cysteine and other reducing agents may have a direct effect on the gluten proteins as well as an effect on the flour enzymes. They stated that the liquefaction of a flour paste is not necessarily due to proteolysis.

Recent work by Hlynka (36) lends support to the view that cysteine, glutathione, bisulfite and sulfide may affect gluten directly. Small amounts of bisulfite added to dough markedly reduced its elasticity and, when glutens were washed from such doughs, they were found to be soft, sticky and inelastic. Bisulfite-like reactions in doughs were produced by cysteine, glutathione and sulfide. Acetaldehyde, which readily forms an addition compound with bisulfite, can prevent bisulfite from affecting dough and gluten when the two reagents are incorporated simultaneously into dough. Further, it can counteract effects in bisulfite-treated glutens. The ready reversibility of bisulfite effects in doughs and gluten is not consistent with a proteolytic hypothesis.

Another theory proposed to explain the beneficial effects of small amounts of certain reagents on the physical properties of flour dough was advanced by Sullivan (65). Sullivan believed that these reagents had a direct effect on the gluten protein of dough by virtue of changes produced in the oxidation-reduction potential. It was stated that no two flour improvers exerted their effects in exactly the same way. Their action, however, was explained by assuming the presence of SH or some similar reducing group in flour. The incorporation of oxidizing agents into dough resulted in a displacement of the system

$$-S-H \rightleftharpoons -S-S-$$

from left to right.

This theory arose from the findings that the harmful effects of fresh wheat germ on baking quality of flour were not primarily due to lipid components (68). These harmful components of germ were shown to be water-soluble (69), and later the presence of glutathione in wheat germ was demonstrated and its harmful effect on baking properties noted (65). Sullivan (66) postulated that the beneficial effect of heat-treatment of flour and of wheat germ was due to auto-oxidation of glutathione, and that the presence of glutathione in wheat germ, rather than any proteolytic enzyme, was responsible for damage to the gluten of dough and for the resultant poor bread made from flour containing wheat germ.

Baker and Mize (5) carried out tests baking bread from doughs mixed in vacuum and in the presence of various gases such as nitrogen, air and oxygen. Tests were made both with and without the presence of potassium bromate and inorganic peroxides. Doughs mixed in air for long periods of time up to 40 minutes were found to become first soft and sticky and later "dead", i.e. to have no elasticity. Loaf volume decreased on prolonged mixing in air and similar results were obtained, although more rapidly, when mixing was conducted in oxygen. It was found that doughs could be mixed for prolonged periods in vacuum and in the presence of nitrogen or hydrogen without apparent damage to the bread. The effect of oxygen on dough properties was said to occur only during mixing.

When doughs containing bromate were mixed in vacuum, the doughs appeared unchanged regardless of mixing time. However, when fermentation took place characteristics developed similar to those occurring with doughs mixed in oxygen. Doughs mixed for short periods of time yielded improved bread, while doughs mixed for long periods of time yielded damaged bread.

Experiments were then made in which doughs were given a period of pre-mixing before bromate was added and then a short subsequent mix after the addition. Bread baked from such doughs had the characteristics of bread made from doughs in which bromate had been present for the whole mixing period. The authors postulated that the mixing action sensitized the dough so that a normal dosage of bromate produced very damaging effects on the bread properties. The sensitized dough responded favorably to a bromate addition of one-tenth the normal dosage.

Freilich and Frey (22) reported that bromate produced effects on dough and bread properties in addition to, and different from, proteolytic inhibition. The action of bromate in dough was illustrated by its effect on loaf volume in the presence of added papain. The deleterious effects of added papain (75 mgm. in a dough made from 100 gm. of flour) were largely overcome by the addition of bromate (50 mgm.). Larger additions of bromate produced a decrease in loaf volume and resulted eventually in effects characteristic of excess bromate, i.e. a very stiff, bucky dough and loaves of poor volume and very coarse texture. The bromate effect thus went beyond a point at which it could be explained as due to retardation of proteolytic activity. It was also demonstrated that an actual improvement in loaf volume could be produced with amounts of bromate usually considered excessive in normal baking practice. This was done in experiments in which the period of fermentation was shorter than in the usual baking procedure. Excess bromate effects were thought to be the result of the combined effects of bromate and fermentation, but it was suggested that bromate may produce changes in dough properties even in the absence of fermentation.

Merritt and Bailey (52) also observed that the effects of bromate concentration and fermentation time on loaf volume were interdependent. For a bromate concentration of 3 mgm. per cent, a rather short fermentation period was necessary to attain the maximum possible loaf volume, while when a bromate concentration of 1 mgm. per cent was used, a much longer fermentation period was required to yield the maximum loaf volume.

Freilich and Frey (23) reported that excess bromate effects in bread made from over-bromated doughs could be avoided by remixing the dough after the fermentation period and prior to forming the loaf. Experiments were conducted by remixing doughs after fermentation for varying periods of time in oxygen, air, and nitrogen. It was found that loaf volume increased to a maximum with increased remixing time independently of the presence of oxygen. After this maximum was attained, loaf volume remained almost constant with further remixing time in nitrogen. For doughs remixed in air, the loaf volume increased to the maximum and then showed a decrease on further remixing. When doughs were remixed in oxygen, an even more drastic fall of loaf volume with increased remixing time was observed. The fact that the maximum loaf volume, on remixing, occurred at the same mixing time despite the varied chemical treatment suggested that this change was due to some physical mechanism. However, the change in loaf volume beyond this optimum could be attributed to physical or chemical changes or both.

Freilich and Frey (24) later reported that the improving effect of bromate on bread properties was not due to the oxidation of glutathione in the dough. They found that the addition of oxidizing agents to doughs overcame the harmful effects on loaf volume and bread texture of added reducing agents, but the effects of the latter on mixing time were not eliminated. They suggested either that reducing matter was not oxidized in the dough or that oxidation and reduction involved independent factors in the dough. They pointed out that the failure of oxidizing agents to react with reducing agents in dough was not difficult to understand since such reactions were not instantaneous even under ideal conditions in solution. Reducing agents, they found, seemed to act on the gluten, but they suggested that oxidizing agents might act on another part of the gluten complex.

Freilich and Frey (25) pointed out that the effects of oxygen on dough development, as indicated by the farinograph, are immediate whereas the effects of proteolytic activity are delayed. This suggested that the effects of oxygen during mixing did not involve protease activity but that the oxygen probably acted on the gluten complex. These authors suggested that an enzymatic oxidation was involved in the changes produced in dough properties by oxygen and oxidizing agents. The protease theory, they stated, may be operative to the extent that protease is present and active in dough, but it must assume a minor role in explaining the effects of oxidation in flour doughs.

The fate of potassium bromate in flour doughs is an interesting subject which has received only brief consideration in the literature. Sullivan, Howe, Schmalz, and Astleford (67) reported investigations on the amount of bromate used at various stages of the bread-making process, Over half of the bromate initially added to the flour, prior to the commencement of mixing, was used up immediately during the mixing process, while a comparatively small amount of bromate was consumed during the course of three hours fermentation. When the baked bread was taken from the oven, no bromate remained.

Recent investigations by Hlynka and Templin (37) have shown that bromate does not disappear, with time, from non-fermenting flour-water doughs.

From the previous review it is apparent that no satisfactory explanation of the improving action of potassium bromate in flour dough has yet been published. This is not surprising, perhaps, since a wheat flour dough represents an exceedingly complex physico-chemical system. This complexity has probably been largely responsible for the empiricism of many of the techniques used by workers studying dough behavior and dough chemistry. To study the chemistry involved in the behavior of some reagent added to dough, an investigator has no alternative but to work with the complex dough mass itself. Attempts may be made to isolate a given dough constituent to study its behavior with the given reagent, but it is never certain that the process of extraction has not altered the material to be studied, nor is it certain that the behavior of such an isolated component is indicative of its behavior in the dough.

For such reasons, it seemed necessary to focus attention on the dough itself in any attempt to study the influence of potassium bromate on dough properties. The main experimental difficulty is one of separating and identifying the measurable physical properties of the dough which are of significance in reflecting the modification of its physico-chemical properties brought about by the incorporation of minute amounts of added reagents.

It was suggested earlier in these introductory remarks that fundamental knowledge of the reaction of potassium bromate in dough might be obtained by regarding the dough as a polymeric material in which the properties were determined by a network structure. On such a premise, changes in the physical properties of dough due to the addition of minute amounts of certain reagents would be presumed to have their origin in changes in the network structure. Obviously, to make such a study a suitable method must be chosen to make measurements of the changes in the physical properties produced by the added reagents.

In recent years, the Brabender Extensograph has been widely used to study dough characteristics and it has been found that measurements with this instrument are quite sensitive to the presence of potassium bromate in the dough (14, 52, 57). Moreover, it appeared to yield a type of measurement that seemed likely to permit of reasonably fundamental analysis. For these reasons, the extensograph was adopted for the present investigation.

EXPERIMENTAL

THE EXTENSOGRAPH

The Brabender Extensograph, an empirically-designed physical dough-testing instrument, has been used to study the reactions of potassium bromate in flour dough. The extensograph, as shown in figure 1, stretches a cylinder of dough of known dimensions, at a constant rate, until the sample breaks and automatically records a load-extension curve for the dough cylinder of decreasing cross-section. This curve, or extensogram as it is called, is largely empirical. Since both elastic and viscous dough properties are involved throughout most of the elongation of the dough, the extensograph can not be expected to provide independent measurements of each. A typical extensogram is shown in figure 2.

The measurements taken from such curves in the routine testing of doughs are these:

(a) the maximum height, L, of the curve, to obtain a measure of the maximum load supported by the dough during the stretching test,

(b) the overall length, E, of the curve, as a measure of the length to which the dough can be stretched before it breaks, and

(c) the area of the curve, which determines the work done in stretching the dough until it breaks.

Measurements of the physical extensograph properties of doughs are quite easily reproducible. Aitken, Fisher, and Anderson (1) state that the standard error of the mean of duplicate curves is of the order of ±0.7 cm. for an average length of 20 cm., and ±0.2 cm. for

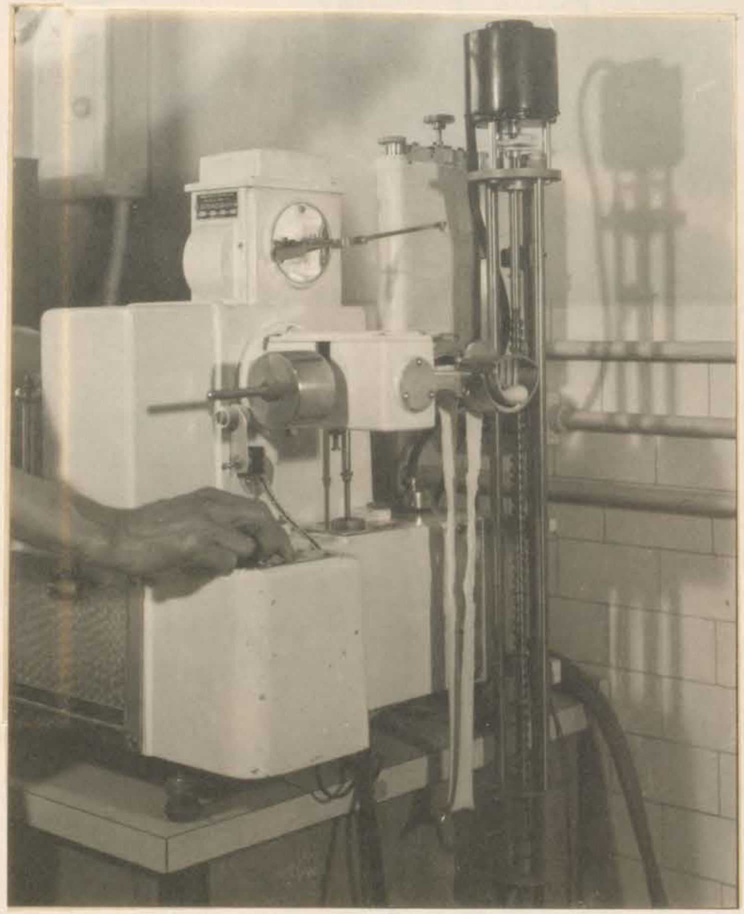


Fig. 1.

The Brabender Extensograph
A test dough is being stretched by the
instrument and the extensogram recorded.

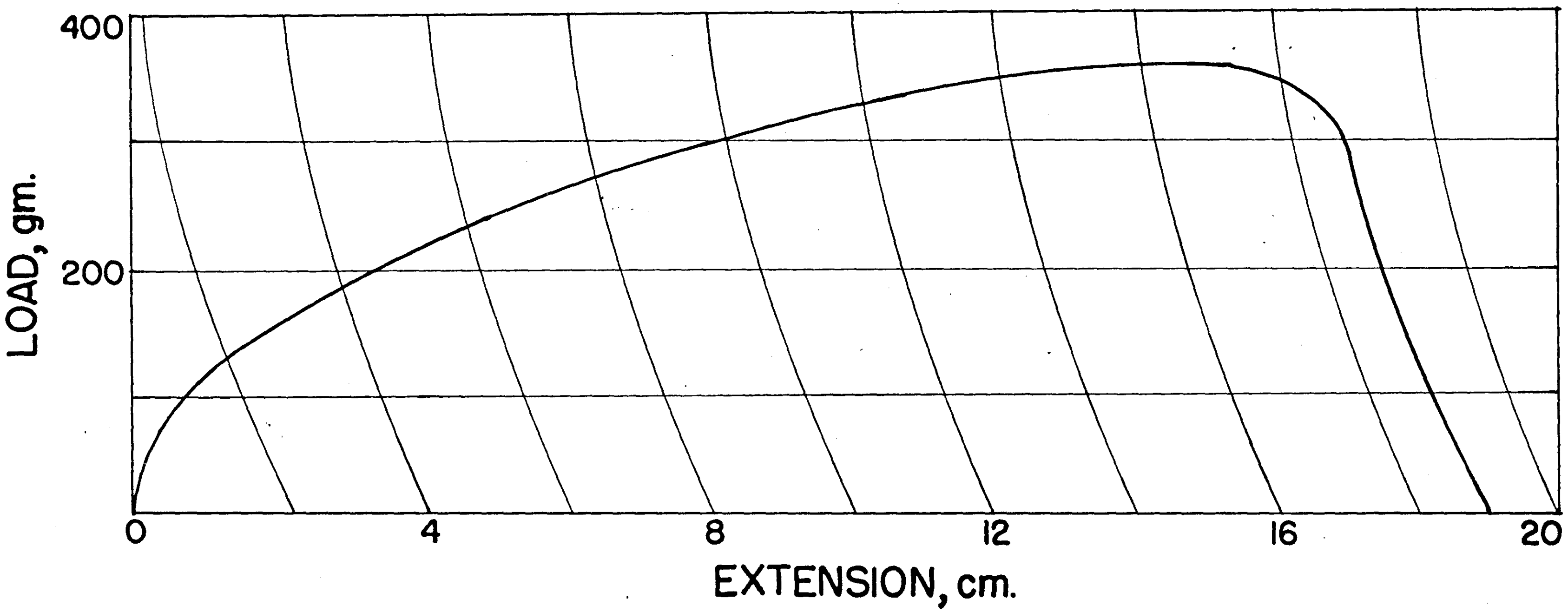


Fig. 2.

A typical extensogram.

an average height of 6.5 cm. These latter measurements correspond to an error of ±10 gm. for an average load supported by the doughs of 370 gm.

A schematic diagram of the extensograph, adapted from Bailey (4), is shown in figure 3. Bailey describes the instrument as follows:

> "The solid cylinder of dough to be tested is shown at 1, supported by an arm, 2. The dough is held by clips, the farther one being shown at 3, while the one at the near end of the dough cylinder has been removed to expose the dough. A mechanism at 4 drives the arm at 5 which engages and extends the dough. As the dough is extended by the motion of this arm, force is exerted which works against the counterweight at the left and registers through the lever system, 6 and 7, to the stylus running on the face of the chart at 8. The greater the force, F, the farther down the chart does the stylus move. The horizontal motion of this chart is synchronized with the motion of the motor, 4, and accordingly registers the distance that the arm, 5, moves in extending the dough".

The extensograph used in this investigation had a paper velocity of 6.8 mm. per second and a hook velocity of 14.6 mm. per second (1). The tension on the balance corresponds to 200 paper units with a balancing weight of 470 gm. This calibration means that one unit on the extensogram load axis is equivalent to 1 gm. The range of the instrument is, on this basis, 0 to 1,000 gm.

In the extensograph ensemble is included not only the actual device indicated in figure 3, but also a "rounding up" device for the preparation, in a standard manner, of round dough masses from the test

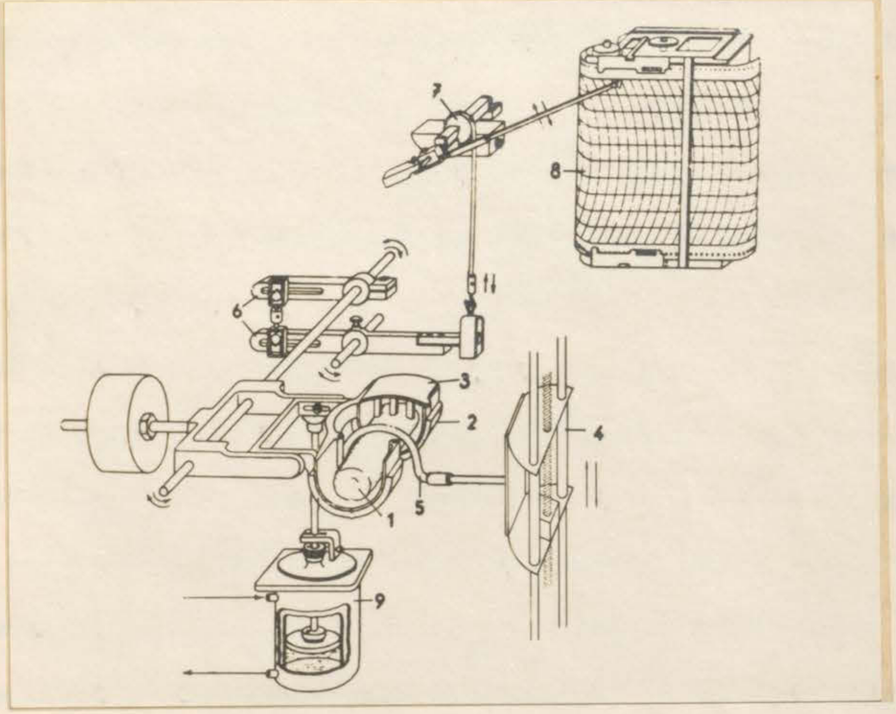


Fig. 3

A schematic diagram of the
Brabender Extensograph.

samples, as well as a "dough molding" device for mechanically preparing, from the round dough masses, the cylindrical test pieces.

The rounder consists of a small, rigidly fixed square box. A movable plate serves as the bottom. In the centre of this plate is a pin which projects upward into the box for about one inch. When the rounder is in operation, this plate moves so that the pin describes a circle inside the rigid box. A weight serves as the top of the box. When a dough is placed in the rounder, the weight or lid is placed on top and impales the dough on the pin. When the rounder is put into operation, the dough is sheared somewhat as the pin inscribes its circle within the box. When a dough is rounded up, the bottom plate is always given twenty revolutions so that the same amount of work is done on every sample.

The dough molding device or roller consists of a revolving central cylinder and an outer concentric drum. When a round dough ball is put into the roller, it is pressed between the revolving central cylinder and the outer one and rolled out into cylindrical shape.

The technique employed when using the extensograph may be described in the following way. A flour dough, of baking absorption, is prepared from 200 gm. flour. This dough is then divided into two 150 gm. portions. A 150 gm. dough sample is placed in the rounder and the base plate given exactly twenty turns. The dough ball thus formed is passed through the roller and emerges in the form of a sausage-shaped cylinder. This test piece is now placed in a dough holder and clamped therein as shown in figure 3. Test samples so prepared are placed in a cabinet with a sensitive temperature control and in which humidity is maintained at 85 per cent to prevent, as much as possible, drying at the surface of the doughs.

Munz and Brabender reported that, if a dough was tested on the extensograph shortly after it had been mixed and shaped, it supported a very high load (55). However, the load supported by a dough decreased rapidly with increasing rest period between shaping the dough cylinder and stretching it on the extensograph. This behavior was due to the mixing and shaping operations, the dough becoming "excited" as a result of the mixing action. However, for rest periods in excess of about forty five minutes, very little further change in load occurred. On the basis of such observations, it was decided that a period of forty five minutes between the shaping operation and subsequent stretching was sufficient to allow doughs to return, from the "excited" state due to working, to a normal unexcited state.

Thus it has become customary, in dough-testing with the extensograph, to mix a dough, mold it into shape on the extensograph, and allow a rest period of forty five minutes before the sample is stretched.

If it is desired to follow the changes with time in extensograph dough properties, the technique used by some investigators has been to mix and shape the dough on the extensograph, allow it a rest period of forty five minutes and then stretch it. Immediately it was stretched, the dough was reshaped on the extensograph and tested again forty five minutes later, i.e. ninety minutes from the time of mixing. This cycle of operations may be repeated over and over as long as it is desired to follow the changes in dough properties.

MATERIALS AND METHODS

The materials used in this investigation consisted, generally, of composite samples of hard red spring wheat, graded 1 Northern and 2 Northern. The samples were milled in an Allis Chalmers experimental mill to a yield of approximately seventy two per cent flour. Six such samples were used in the course of this study. The moisture content, protein content, and absorption of these six samples are recorded in Table I. Protein determinations were made on the samples according to the Kjeldahl method. The values are recorded as Nitrogen x 5.7 and have been corrected to a 14 per cent moisture basis. Flour absorption was determined using the farinograph by adding sufficient water to 50 gm. flour containing 14 per cent moisture, or its equivalent, to give a dough consistency corresponding to 540 farinograph units.

TABLE I

MOISTURE CONTENT, PROTEIN CONTENT, AND ABSORPTION OF FLOUR

Sample	Moisture content %	Protein content, % 14 % moisture basis	Absorption, % 14 % moisture basis
A	13.1	13.1	62.6
B	12.6	-	63.4
C	13.2	13.3	64.0
D	13.2	13.5	63.8
E	13.7	13.2	61.0
F	13.8	13.2	61.4

The manufacturer recommends that doughs, to be tested on the extensograph, be mixed in the farinograph to ensure uniform treatment of the test pieces. The selection of the farinograph for mixing test doughs appears to be an arbitrary one for which the literature contains no support. All of the flour doughs used in this study were prepared by mixing the dough ingredients in a specially-designed G. R. L. mixer. This mixer is designed so that flour doughs can be mixed in air, in vacuum, or in any other gaseous atmosphere should need arise. The dough ingredients, i.e. flour and doughing liquid, were temperature-conditioned overnight prior to use so that the doughs were taken from the mixer at a temperature of 30°C (unless otherwise stated). All doughs were mixed to contain 1 per cent sodium chloride, i.e. 1 gm. salt in each 100 gm. flour on a 14 per cent moisture basis. Salt is a necessary dough ingredient since it has been found that, without it, many doughs become too sticky for convenient manipulation during the extensograph tests, (14).

All of the chemicals employed in this investigation, viz. sodium chloride, potassium bromate, and cupric chloride, were of reagent grade and were used directly as supplied. These salts were each dissolved, in appropriate concentration, in distilled water, and added, in the required concentrations to the flour samples just as mixing was about to be commenced. Unless otherwise specified, a constant mixing time of three minutes was employed throughout the course of the work.

Some experiments were conducted in which doughs were mixed in an atmosphere other than air, i.e. in nitrogen and in oxygen. For these experiments, the following technique was employed. Weighed flour samples were placed in vacuum desiccators, and the pressure in the desiccators reduced to about 1 cm. of mercury to remove any gases adsorbed on the flour particles. This reduction of pressure was accomplished in about 5 minutes with a Megavac pump. Attempts were not made to reduce the pressure further by increasing the time, since this would be liable to bring about a change in the moisture content of the flour. Pressure in the desiccator was then restored to atmospheric by admitting the appropriate gas, either nitrogen or oxygen. This cycle of reduction of pressure, etc. was repeated three times. The flour samples in an atmosphere of the appropriate gas were then temperature-conditioned overnight prior to use. Just before mixing, each flour sample was placed in the bowl of the mixer and the mixer evacuated to a pressure of about 2.5 cm. of mercury. Immediately, the pressure was restored to atmospheric by leading into the mixing chamber the appropriate gas. The required amount of the doughing liquid was then run into the mixing chamber and the mixing commenced. During the mixing process, a gentle stream of the gas flowed through the mixing chamber at atmospheric pressure.

RESULTS

Preliminary Experiments

The experimental technique recommended by the Brabender Corporation for extensograph testing of flour doughs appears to be arbitrary and was modified somewhat at the outset of this work. Flour doughs were mixed from 200 gm. samples of flour for three minutes in the G. R. L. mixer and from each such parent dough, two 150 gm. portions were taken. Some of these were immediately rounded and rolled into the required cylindrical test samples and then clamped in the dough holders. After these samples had rested for a period of 45 minutes at a temperature of 30°C and at a relative humidity of 85 per cent, they were stretched on the extensograph. Other dough samples were not rounded immediately, but were placed in the temperature- and humidity-controlled cabinet for time intervals which were multiples of 45 minutes. Some of these samples were taken from the cabinet 45 minutes after mixing, some 90 minutes after, and so on. These samples were then rounded and rolled on the extensograph, rested for 45 minutes and stretched. In this way extensograph tests were made on dough samples of increasing age, with each sample shaped on the extensograph 45 minutes before it was tested.

When this technique is applied to untreated control doughs and to doughs containing 3 mgm. per cent potassium bromate (i.e. 3 mgm. bromate per 100 gm. flour on a 14 per cent moisture basis), typical results in terms of the extensograms are as shown in figure 4.

Figure 4 shows that with untreated control doughs, increased reaction time from mixing until testing resulted in very little change in the physical extensograph properties, except perhaps a slight decrease in the load supported.

With increasing reaction time for bromate-treated doughs, a considerable change in the extensograph dough properties occurred. Initially, there was found to be very little difference between the extensograph properties of untreated and bromate-treated doughs, but as the reaction time was increased, a progressive difference in the properties developed. The extensograms obtained for the bromate-treated doughs became progressively shorter and higher, i.e. the doughs became progressively less extensible and able to support an increased load when stretched.

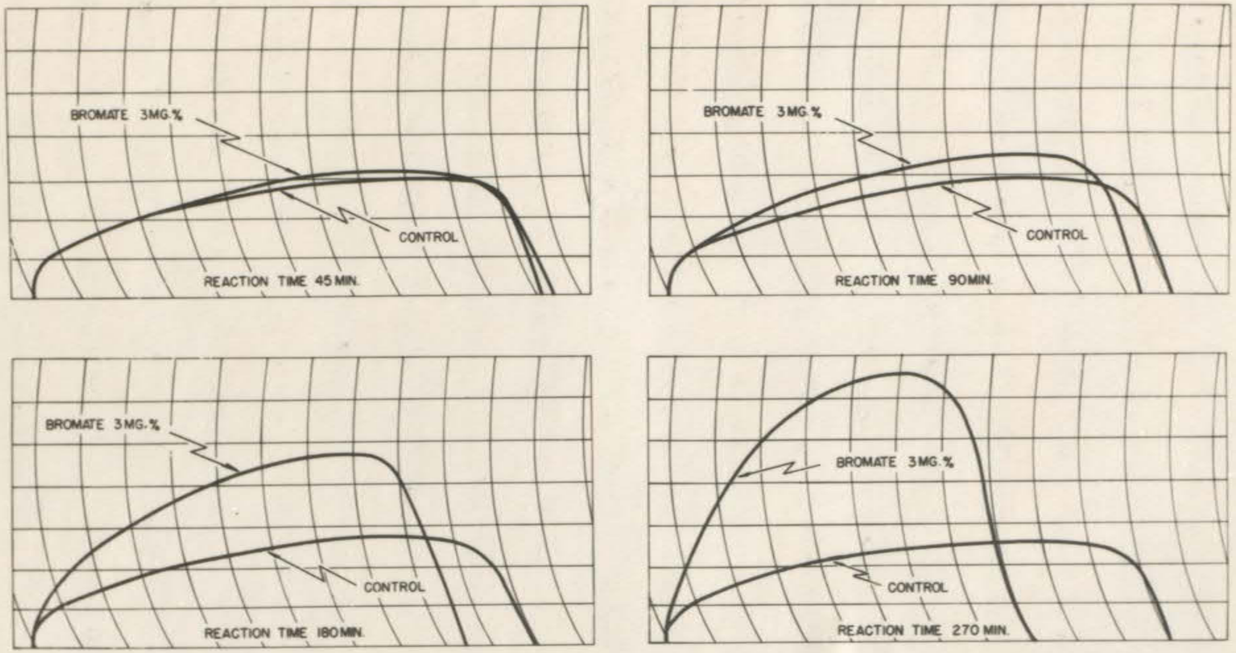


Fig. 4.

Extensograms showing the progressive changes produced in dough properties by potassium bromate.

The changes in the physical properties of flour doughs due to the action of potassium bromate over a period of time were also quite evident in comparative subjective tests. Such tests, of course, are not very precise. A bromate-treated dough two hours old required considerably more force to stretch it in the hands than an untreated dough of the same age. Then, too, when the stretching force was removed, the bromate-treated dough showed a much greater tendency than the untreated dough to undergo elastic recovery. Again, a bromate-treated dough, when rounded into a ball after two hours reaction time, exhibited much less tendency to flow, i.e. flatten out, than an untreated dough treated in the same manner.

The analytical treatment applied to experimental extensograms has varied. Munz and Brabender (55, 56, 57) analyzed their extensograms by noting the maximum load supported by a dough and by measuring the extension of the dough when it broke. These authors condensed their data by reporting these factors as the ratio of load to length. Other investigators (1, 52) have preferred to use just the load at the maximum of the extensogram.

It can be seen from the extensograms in figure 4 that, at any given reaction time, the maximum load supported by a bromate-treated dough did not generally occur at the same dough extension as the maximum load supported by an untreated dough. Further, it can be seen, that the maximum load supported by bromate-treated doughs, with increasing reaction time, did not occur at a fixed extension. Rather, the maximum load occurred at progressively shorter extensions, the greater the reaction time.

It was felt that a more significant measurement than the load at the maximum of the extensogram curve would be the load supported by any dough at some value of constant deformation. The measurement of load then becomes somewhat equivalent to a measurement of stress since a constant sample deformation should correspond closely to a constant cross-sectional area. This method of obtaining results at constant sample deformation has been widely used in the study of rubber and other elastomers. The fact that the shape of the extensogram is determined in part by a changing sample cross-section as extension progresses should not influence the interpretation of results calculated in this manner.

In the present study, all extensograms were analyzed in the following manner. From the extensograms were read the load supported by the doughs at a constant sample extension of 11 kimograph cm. This extensogram extension corresponds to an actual dough length of about 60 cm. and represents a dough extension of about 400 per cent. The particular value of 11 cm. extensogram extension was chosen arbitrarily, but it will be shown later that the arbitrary selection of this particular value for constant sample deformation does not significantly influence the subsequent interpretation of the experimental data. It may be noted that the maximum extensogram height was rarely observed at extensions of less than the 11 cm. value.

Some preliminary experiments were made using the modification of the routine Brabender extensograph technique to assess the changes in the physical properties of bromate-treated doughs with time. Flour doughs were prepared from Sample A to contain respectively 0, 1, 2, 3, 4, and 5 mgm. per cent potassium bromate. These doughs were made by mixing 200 gm. samples of flour to baking absorption after which each dough was divided into two 150 gm. portions for duplicate tests on the extensograph. Doughs of each bromate concentration from 0 to 5 mgm. per cent were allowed increasing reaction times from 0 to 270 minutes using 45 minute intervals. Each dough was shaped on the extensograph, for the first time, 45 minutes before it was to be stretched. In other words, a dough allowed no reaction time was tested when it was 45 minutes old and a dough allowed a reaction time of 180 minutes was tested when it was 225 minutes old. The extensograms obtained in this experiment were analyzed by reading at 11 cm. extension the load in grams supported by the doughs of each bromate concentration at each particular dough age. These data are recorded in Table II and plotted in figure 5.

TABLE II

THE EFFECT OF REACTION TIME ON "45 MINUTE" EXTENSOGRAM PROPERTIES OF DOUGHS CONTAINING POTASSIUM BROMATE

Dough age min.	Load, gm., at 11 cm. extension					
	Bromate concentration, mgm. per cent					
	0	1	2	3	4	5
45	250	255	260	260	270	280
90	245	265	280	305	310	335
135	245	270	310	340	385	420
180	230	265	330	410	555	590
225	235	270	375	510	665	820
270	220	290	425	625	790	-
315	-	320	495	715	-	-

From the lowest curve in the figure, it is evident that there was

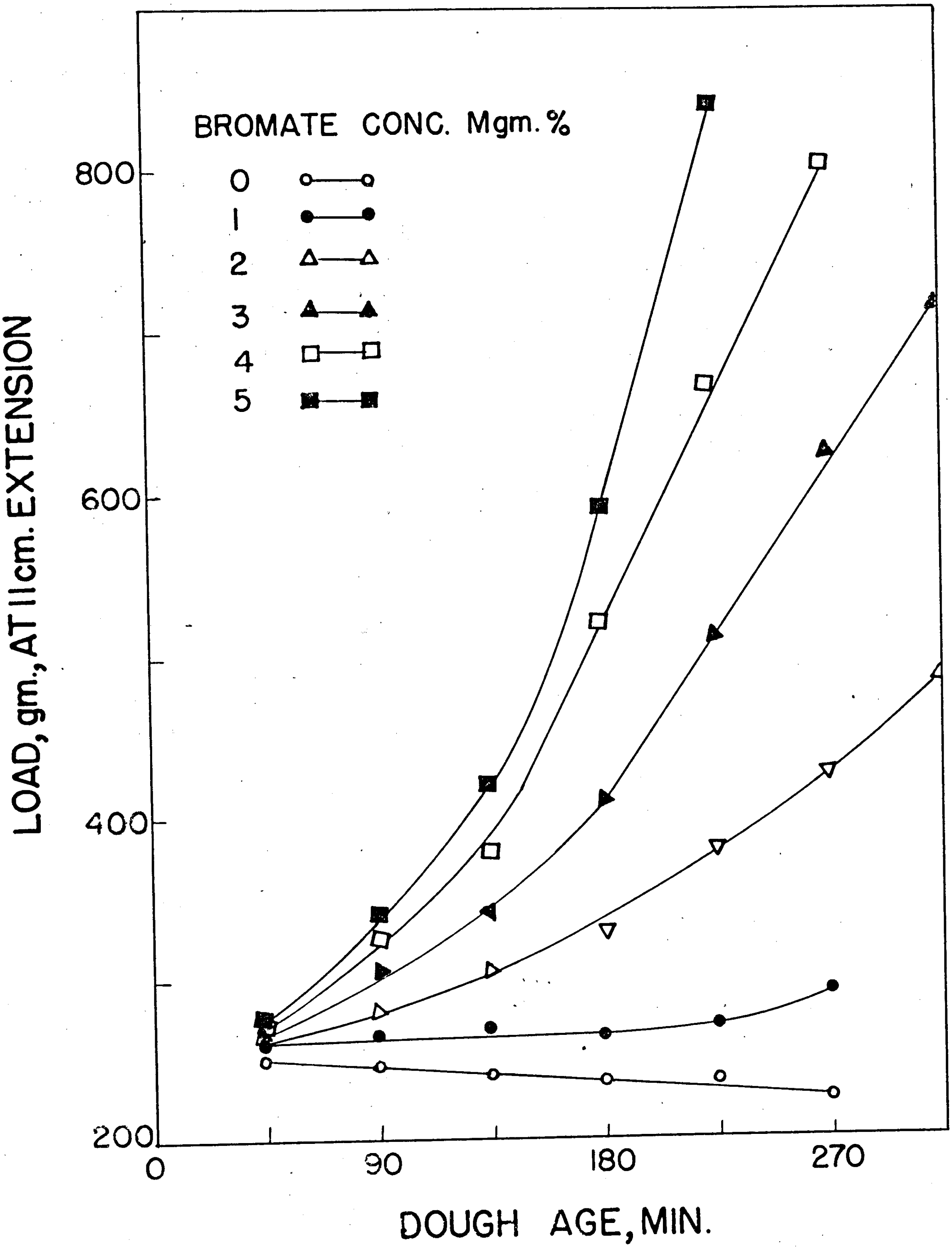


Fig. 5.

The effect of increasing dough age on the extensogram load supported by doughs containing increasing amounts of potassium bromate.

little change in the extensograph properties of untreated doughs with time. However, the incorporation of minute amounts of potassium bromate into the doughs resulted in marked changes in the physical properties of doughs as assessed by the extensograph. The reaction of bromate appeared to take place progressively and continuously with time, bromate concentration being the limiting factor.

The fact that the changes in the dough properties, over the range of bromate concentrations used, continuously increased with increasing concentration is interesting. This is contrary to the effects produced by successive increments of bromate on the properties of baked bread. It is observed that, when a given flour is baked with successive increments of bromate, the loaf volume increases at first to a maximum at a certain level of bromate, but further addition of bromate results in a gradual decline of loaf volume. The optimum bromate concentration for a flour such as Sample A would be in the range of 1 to 3 mgm. per cent, but no optimum was observed in this range for the extensograph measurements with non-fermenting doughs.

Another preliminary experiment illustrated two very important characteristics of the bromate reaction in flour dough. These were:

(a) for the bromate reaction to take place, as indicated by changes in the physical properties of dough, a reaction time between mixing the dough and shaping it (i.e. rounding and rolling it on the extensograph) must be allowed,

(b) for the bromate reaction to be reflected in the physical properties of doughs tested on the extensograph, work must be done on the dough by rounding and rolling after the given reaction time has elapsed.

These factors were demonstrated in the following experiment. Two series of untreated control doughs and two series of doughs containing 5 mgm. per cent bromate were prepared at a temperature of 30°C using flour Sample B. One series of control doughs and one series of the bromate-treated doughs were shaped on the extensograph immediately after mixing, i.e. no reaction time was allowed between mixing and shaping, but they were permitted different rest periods of from 5 minutes to 180 minutes between shaping and stretching. The other control and bromate-treated doughs were set aside immediately after mixing and allowed a reaction time of three hours at 30°C and at 85 per cent relative humidity, after which they were rounded and rolled on the extensograph, and allowed rest periods of from 10 to 180 minutes before extensograms were taken.

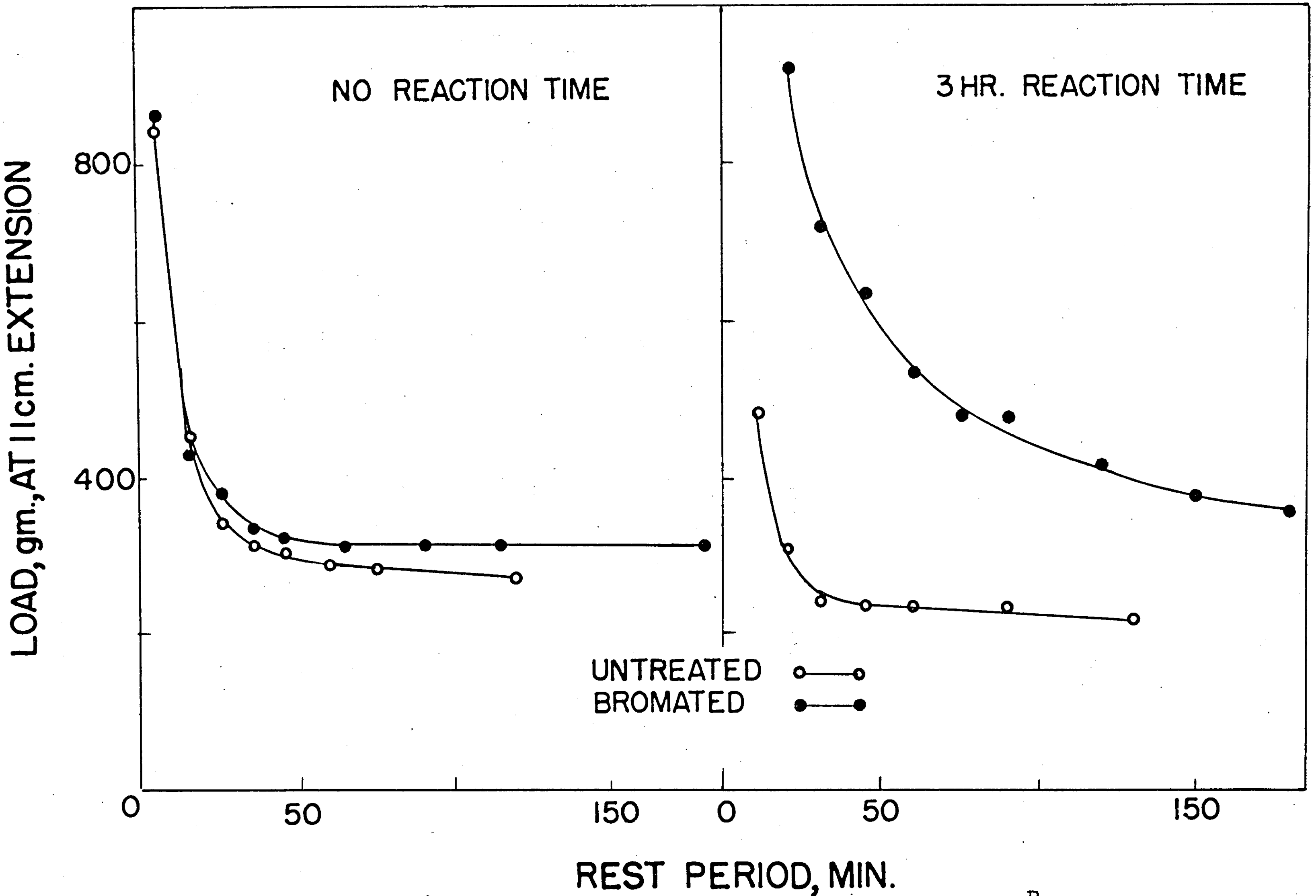
The loads, in grams, at 11 cm. extension of the various doughs are recorded in Table III and plotted in figure 6 where the load is plotted against rest period measured from the end of the reaction time. This gives rise to two sets of curves, one for the control and bromate-treated doughs allowed no reaction time and another for the control and bromate-treated doughs allowed three hours reaction time.

Figure 6 shows that doughs stretched on the extensograph soon after they were shaped were capable of supporting very high loads, but as the length of the rest period between shaping and stretching was increased this load decreased very rapidly. It may also be seen that (figure 6A), with the untreated doughs, this rapid decrease of load was succeeded by an almost linear decrease of load with time. For no

TABLE III

THE EFFECT OF REACTION TIME ON THE CHANGE OF LOAD WITH REST PERIOD FOR UNTREATED AND BROMATED DOUGHS

Rest period min.	Load, gm., at 11 cm. extension			
	0 Reaction time		3 hour reaction time	
	Bromate conc., mgm. %		Bromate conc., mgm. %	
	0	5	0	5
5	840	860	-	-
10	-	-	483	-
15	450	428	-	-
20	-	-	310	920
25	340	380	-	-
30	-	-	242	720
35	310	332	-	-
45	300	320	240	637
60	284	-	237	545
65	-	310	-	-
75	280	-	-	480
90	-	-	235	480
120	270	-	-	422
130	-	-	220	-
135	-	310	-	-
150	-	-	-	382
180	-	310	-	360



A

B

Fig. 6.

Curves showing the effect of reaction time on the change, with increasing rest period, in the extensogram load at constant sample deformation for untreated and bromated doughs.

reaction time, there was little difference between the rate of decrease of load with rest period of the control and bromated doughs. For no reaction time with bromated doughs the load supported by a stretched dough decreased to a value of about 310 gm. when a rest period of 60 minutes was allowed between shaping and stretching. Further extensograms obtained on such bromated doughs with increasing rest period were identical regardless of the length of the time between the shaping and stretching operations. The presence of bromate in dough thus prevented the slow linear decrease of load that was observed for untreated control doughs with increasing rest period in excess of about 45 minutes.

Another result of the presence of bromate in dough may be seen by referring to the curves (figure 6B) for the change of load with rest period when the doughs were allowed a three hour reaction time between mixing and shaping. For the control doughs, the rate of change of load was about the same after a reaction time of three hours as it was after no reaction time. For bromate-treated doughs, however, the rate of change of load with rest period was vastly different with and without the time of reaction. This difference in extensograph dough behavior was only observed with doughs that were shaped or manipulated after a reaction time had been allowed.

From figure 6, it can be seen that in a rest period of 45 minutes, the load supported by unbromated doughs and bromated doughs, shaped immediately after mixing, passed through the stage of rapid decrease. The same may be said of the control or untreated doughs when a three hour reaction time, between mixing and shaping, was allowed.

The physical properties of the untreated doughs regardless of reaction time became more or less stabilized during a 45 minute rest period, and comparatively little change occurred with further rest period. Obviously, however, with bromated doughs that had been allowed a three hour reaction time the load decreased much more slowly during the rest period, and considerable change in the load occurred after the rest period of 45 minutes. Hence, an extensogram obtained 45 minutes after shaping a bromated dough that has been given a reaction time may be largely without meaning, since the dough properties may change drastically with increased rest period.

From the above results it appeared that the routine extensograph technique, i.e. the use of 45-minute extensograms, was not a sound method for following the changes in dough properties due to the action of bromate. However, the same experiments on which this conclusion was based suggested a method which has proved useful in studying the changes in dough properties due to the action of bromate. This consisted of a study of the manner in which bromate affected the rate of decrease of load, with increasing reaction time.

Revised Experimental Method

The experimental technique adopted to study the changes produced in the physical extensograph dough properties due to the reaction of bromate was as follows. Flour doughs were prepared by mixing the ingredients, flour, water, and salt in solution, in the G. R. L. mixer for three minutes. Prior to being mixed, the ingredients were temperature-conditioned so that the doughs, when mixed, would have a temperature of 30°C. Immediately after mixing, doughs of 150 gm. were weighed out and set aside, at a temperature of 30°C and 85 per cent relative humidity, for a given length of time referred to as the Reaction Time.

At the end of the desired reaction time, the doughs were rounded and rolled on the extensograph and then allowed rest periods of from 5 minutes to 180 minutes or more before being stretched on the extensograph. During the rest period, the test pieces were maintained at 30°C and 85 per cent relative humidity.

The experimental extensograms were analyzed, as before, by reading off the values of the load supported by the various doughs at 11 cm. extensogram extension. The data, so obtained, were recorded graphically by plotting load against rest period for each of the various reaction times. The rate of change of load with rest period, as revealed by such plots of extensogram data, will be referred to as Relaxation in the dough.

The Effect of Increasing Reaction Time on the Relaxation of Untreated Control Doughs

To provide a basis of reference from which the changes in the physical properties of doughs due to the incorporation of potassium bromate could be assessed, an experiment was made to determine the relaxation of load with rest period in untreated doughs after various reaction times. Flour Sample C was used in this experiment. Five series of doughs were mixed in the G. R. L. mixer and these were allowed reaction times of 0, 1, 2, 3, and 4 hours between the mixing and shaping operations. At the end of a given reaction time, the doughs were shaped on the extensograph and then allowed various rest periods before being stretched. The data so obtained are recorded in Table IV and represented graphically in figure 7.

TABLE IV

THE EFFECT OF REACTION TIME ON THE RELAXATION OF LOAD SUPPORTED BY UNTREATED DOUGHS

Rest period min.	Load, gm., at 11 cm. extension				
	Reaction time, hr.				
	0	1	2	3	4
5	895	930	945	855	795
10	615	612	580	535	535
15	487	452	437	430	430
20	432	400	375	355	355
30	382	342	347	320	320
40	340	315	305	287	288
50	318	300	300	268	270
75	305	285	275	270	270
100	300	275	272	260	260
125	297	280	282	257	258
150	283	260	265	255	255
175	287	265	268	230	230

The data for the control doughs plotted in figure 7 show the same characteristics as the corresponding curves of figure 6. With increasing rest period between shaping and subsequent stretching, the load decreased quite rapidly at first from very high values, followed by a slower, almost linear, decrease of load. The data for the various reaction times were very nearly superimposed on one another. Thus, the rate of change of load with rest period, i.e. the rate of relaxation, for untreated control doughs appeared to be the same regardless of the reaction time allowed between mixing and shaping the doughs.

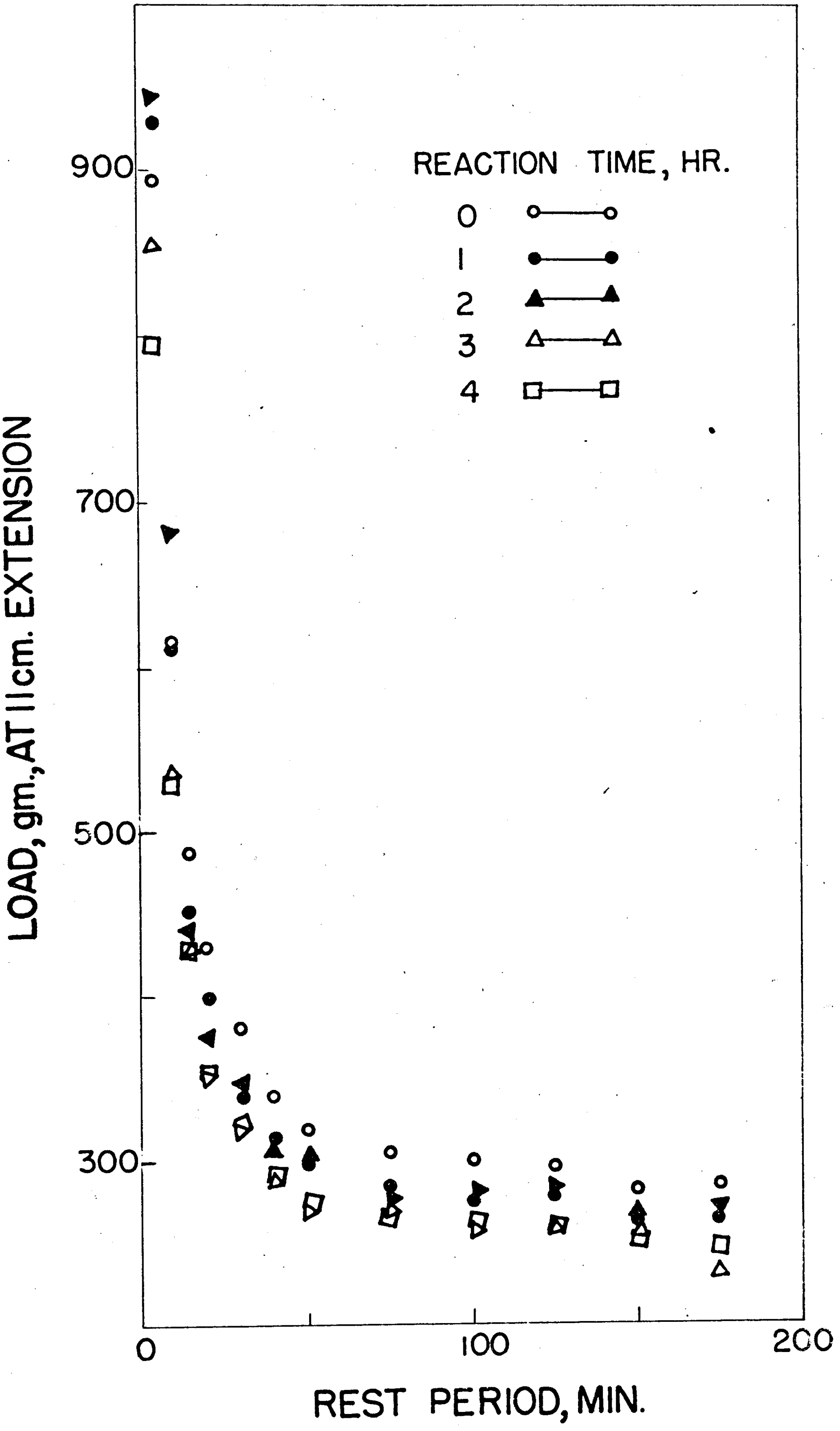


Fig. 7.

Data illustrating the effect of reaction time on the relaxation of load in untreated doughs.

The Effect of Increasing Reaction Time on the Relaxation of Bromate-treated Doughs

To investigate the changes produced in the physical extensograph properties of doughs due to the addition of bromate, experiments were made with the same sample of flour (C) according to the procedure previously outlined. Two series of doughs were prepared containing 3 and 5 mgm. per cent potassium bromate, i.e. 3 or 5 mgm. bromate in each 100 gm. flour. Doughs containing 3 mgm. per cent bromate were allowed reaction times of 0, 1, 2, 3, and 4 hours between mixing and shaping the doughs, and doughs containing 5 mgm. per cent bromate were allowed reaction times of 0, 1, 2, and 3 hours. At the end of a given reaction time, the doughs were shaped, allowed various rest periods, and then stretched on the extensograph. The data are recorded in Table V and plotted in figure 8.

Figure 8 illustrates the pronounced effect produced by bromate, with increasing reaction time, on the physical extensograph properties of doughs. With increasing reaction time, bromate resulted in a decreased rate of change of load, i.e. a decrease in the rate of relaxation. This effect of bromate on dough properties with increasing reaction time is more pronounced the greater the bromate concentration in the dough. Moreover, with increased rest period, the load decreased to a stable value, the particular value depending on the bromate concentration and reaction time. For a given bromate concentration the final stable value of load was higher the longer the reaction time, while the increase in final value of load was more rapid with increasing reaction time at the higher concentration of bromate.

TABLE V

THE EFFECT OF REACTION TIME ON THE RELAXATION OF LOAD SUPPORTED BY BROMATED DOUGHS

Rest period min.	Load, gm., at 11 cm. extension								
	3 mgm. % bromate					5 mgm. % bromate			
	Reaction time, hr.					Reaction time, hr.			
	0	1	2	3	4	0	1	2	3
5	985	-	-	-	-	965	-	-	-
10	603	840	-	-	-	610	885	-	-
15	520	630	770	930	-	-	755	-	-
20	460	505	700	-	980	482	690	-	-
25	-	447	545	735	-	418	570	815	-
30	405	-	-	-	788	-	-	-	-
35	-	-	505	640	-	390	485	745	-
40	347	410	-	-	685	-	-	-	880
45	-	-	430	560	-	350	440	650	-
50	340	368	-	-	625	-	-	-	860
60	-	-	-	475	-	338	410	520	-
65	-	-	-	-	-	-	-	-	785
75	320	335	377	468	520	330	370	510	-
90	-	-	-	-	-	-	-	-	730
100	310	328	380	387	472	322	370	485	-
115	-	-	-	-	-	-	-	-	650
125	310	317	338	435	430	-	365	490	-
140	-	-	-	-	-	-	-	-	670
150	315	340	365	405	450	-	360	460	-
165	-	-	-	-	-	-	-	-	632
175	305	318	355	370	430	-	370	430	-
190	-	-	-	-	-	-	-	-	630
200	-	335	365	390	410	-	-	430	-
215	-	-	-	-	-	-	-	-	590
225	-	-	-	390	410	-	-	430	-
240	-	-	-	-	-	-	-	-	560

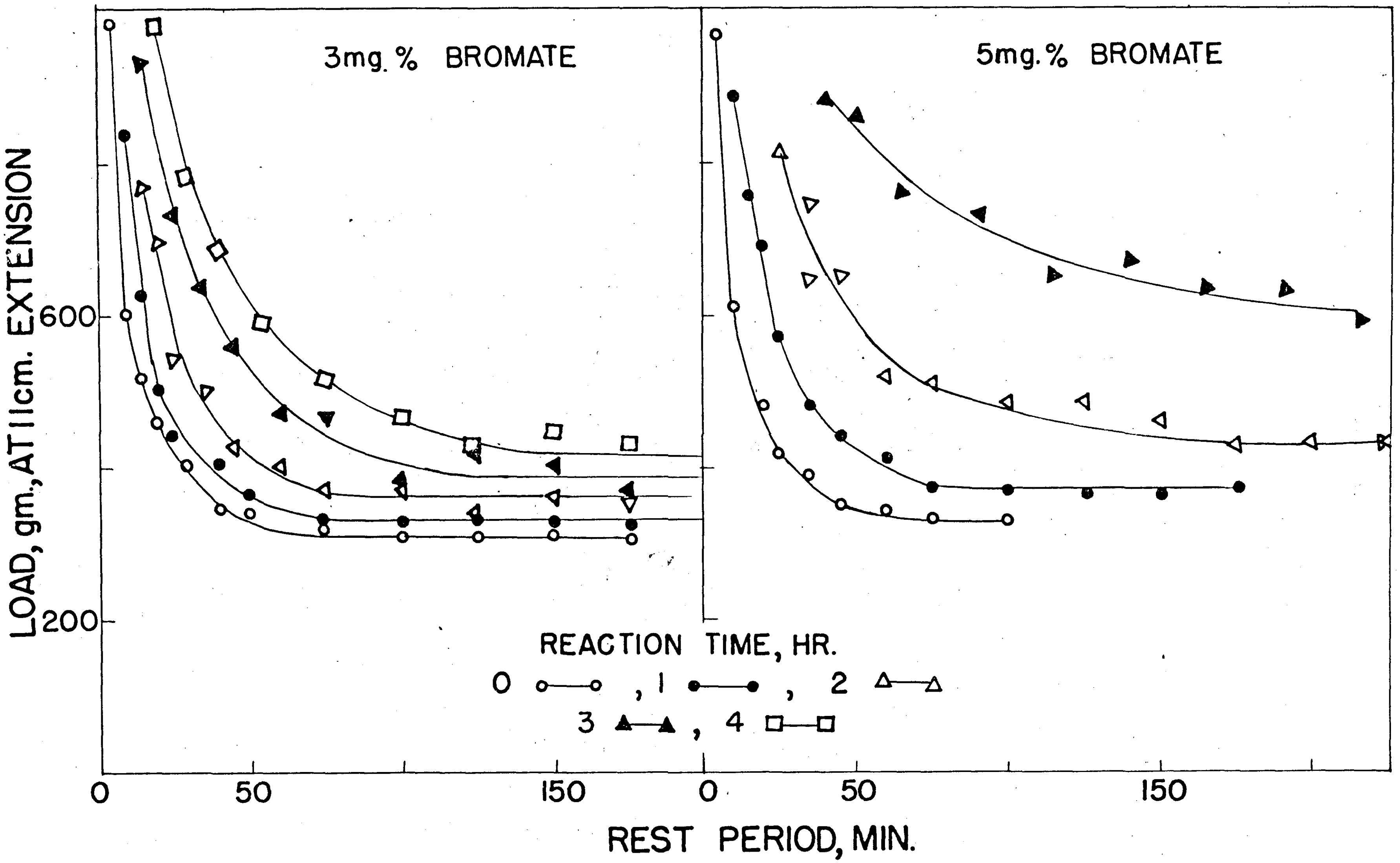


Fig. 8.

Curves showing the effect of reaction time on the relaxation of load in bromate-treated doughs.

The shape of the relaxation curves in figure 8 suggested that the decrease of load with increasing rest period for these doughs obeyed an exponential decay law, although the decay did not continue to zero load. Calculations were made to determine whether the decay of load with rest period was actually exponential. For each relaxation curve of figure 8, load values were corrected by subtracting the residual load at the limit of decay. The values of the final load used to apply the correction for each reaction time are recorded in Table VI. A plot of $\log_{10}$ of the "corrected" load was made against the rest period for each bromate concentration and each reaction time. As figure 9 shows, this relation is linear over a considerable range of rest periods for each bromate concentration at each reaction time. The slope of each of the lines of figure 9 was determined as a measure of the rate of decay of load for each of the various reaction times at each bromate concentration and, since common logarithms were used, multiplication of each of these values by the appropriate factor yields the relaxation constant, k. These values are also recorded in Table VI.

A plot of the rate of relaxation, k, against reaction time for both the 3 and the 5 mgm. per cent bromated doughs is given in figure 10 from which it appears that the rate of relaxation of load decreased linearly with increasing reaction time for a given bromate concentration. Apparently the change in the rate of relaxation occurred more rapidly at the higher bromate concentration. Since the rate of relaxation of load changed linearly with increasing reaction time in bromated doughs, the reaction of bromate in dough may be

TABLE VI

FINAL LOAD, SLOPE OF CORRECTED LOG. PLOT, AND RELAXATION CONSTANT FOR BROMATED DOUGHS

Reaction time hr.	Bromate concentration mgm. %	Final load gm.	Slope of corrected log. plot	Relaxation constant k
0	3	310	-0.0229	0.0529
1	3	330	-0.0189	0.0435
2	3	350	-0.0182	0.0419
3	3	400	-0.0156	0.0359
4	3	420	-0.0138	0.0317
0	5	320	-0.0246	0.0566
1	5	370	-0.0160	0.0369
2	5	430	-0.0122	0.0282
3	5	500 x	-0.00433	0.00997

x Final load estimated from the relaxation data since a stable value had not been attained within the rest periods allowed

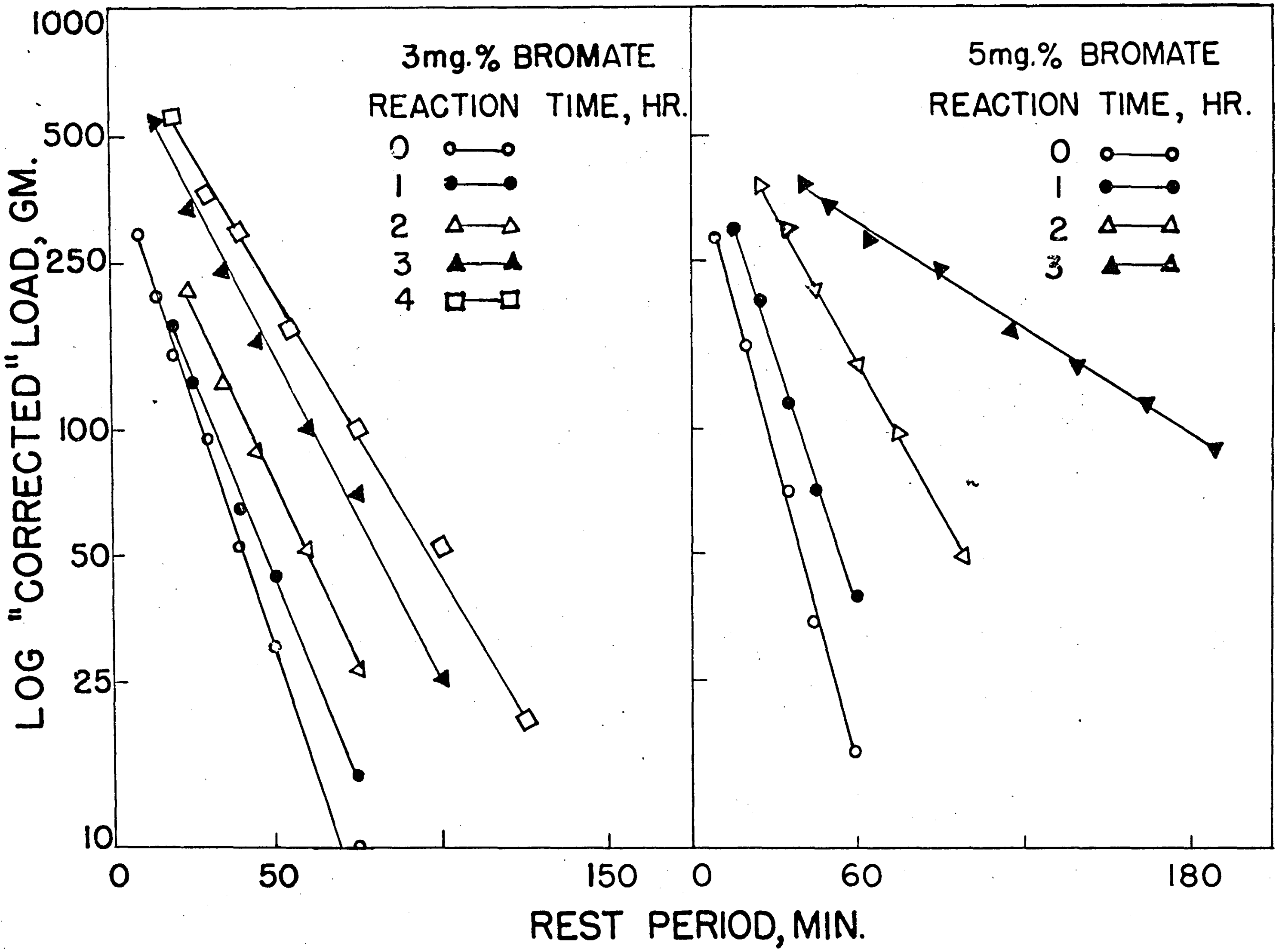


Fig. 9.

Curves showing the exponential decay of load with increasing rest period for bromated doughs of various reaction times.

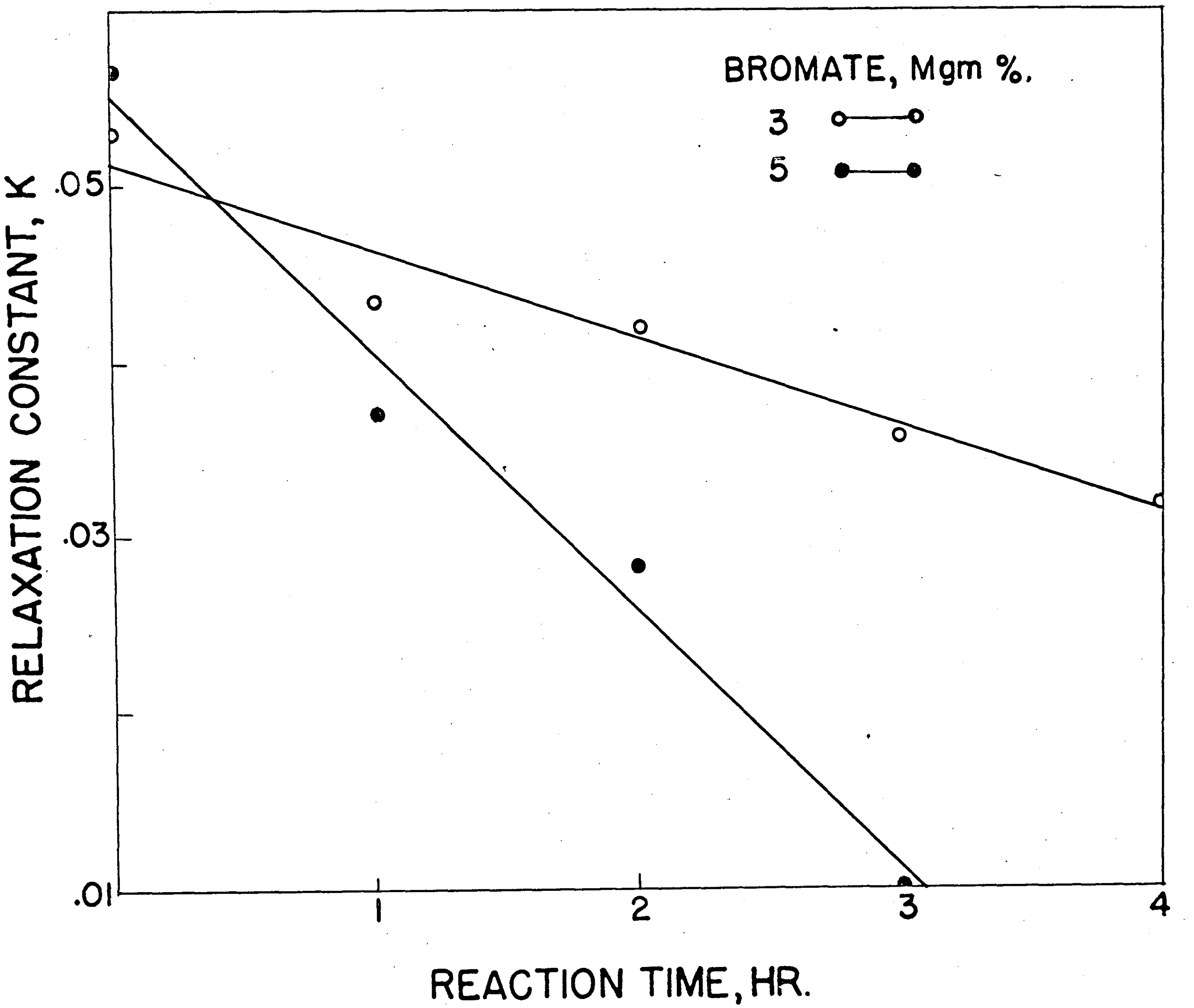


Fig. 10.

Curves showing the effect of increasing reaction time on the rate of relaxation in bromated doughs.

regarded as kinetically of zero order.

The Effect of Elongation on the Analysis of Extensogram Data Obtained in Relaxation Experiments

The data presented in the previous sections were obtained from experimental extensograms by reading off the load supported by the various doughs at a constant, arbitrarily chosen extension of 11 cm. corresponding to constant deformation of the sample. This differs from the procedure generally employed in analyzing extensograms where the load at the maximum of the curve is taken. It was obviously a point of interest to determine whether the methods of analysis yielded essentially the same information about the effect of bromate in dough.

The extensograms obtained in the relaxation experiments were therefore reviewed and the load supported by these doughs noted for 3, 7, and 11 cm. extensogram extensions together with the load at the maximum of the extensograms. The latter, of course, do not occur at a constant extension. For a given relaxation experiment, these data gave rise to four curves when load was plotted against rest period, i.e. one curve for each of the three values of constant extension and one for the load at the maximum. The extensograms of a large number of relaxation experiments gave results, by the different methods of analysis, which were essentially the same from one experiment to another. Some typical values are recorded in Table VII and plotted in figure 11A.

The relaxation curves of figure 11A all show essentially the same behavior of a more or less rapid initial decrease of load with rest period to a stable value of load at longer times. The curves are, of course, displaced from one another along the y- or load axis according to the elongation at which the load was measured.

TABLE VII

THE EFFECT OF ELONGATION ON THE LOAD SUPPORTED BY BROMATED DOUGHS IN A RELAXATION EXPERIMENT

Rest period min.	Load, gm., at			
	Maximum	11 cm.	7 cm.	3 cm.
22.5	940	890	640	275
30	860	732	535	250
40	765	645	460	240
60	642	547	428	228
75	620	495	377	210
90	600	475	360	213
105	607	435	320	200
120	560	413	308	190
150	567	420	310	190
180	590	450	335	-
205	535	405	308	190

Correction of the relaxation curves of figure 11A was made in the manner previously described, i.e. by subtracting the final load value for a given curve from each point on that curve, and a logarithmic plot of the corrected load against rest period was made for each value of constant deformation. These corrected log. plots are shown in figure 11B.

The logarithmic plot of the corrected load against rest period was linear over a considerable range of rest periods for each of the different elongations. The linearity of the logarithmic plots confirms, as before, the exponential decay of load with rest period. Of further interest is the fact that the lines obtained for the three different values of constant elongation were virtually parallel (cf.

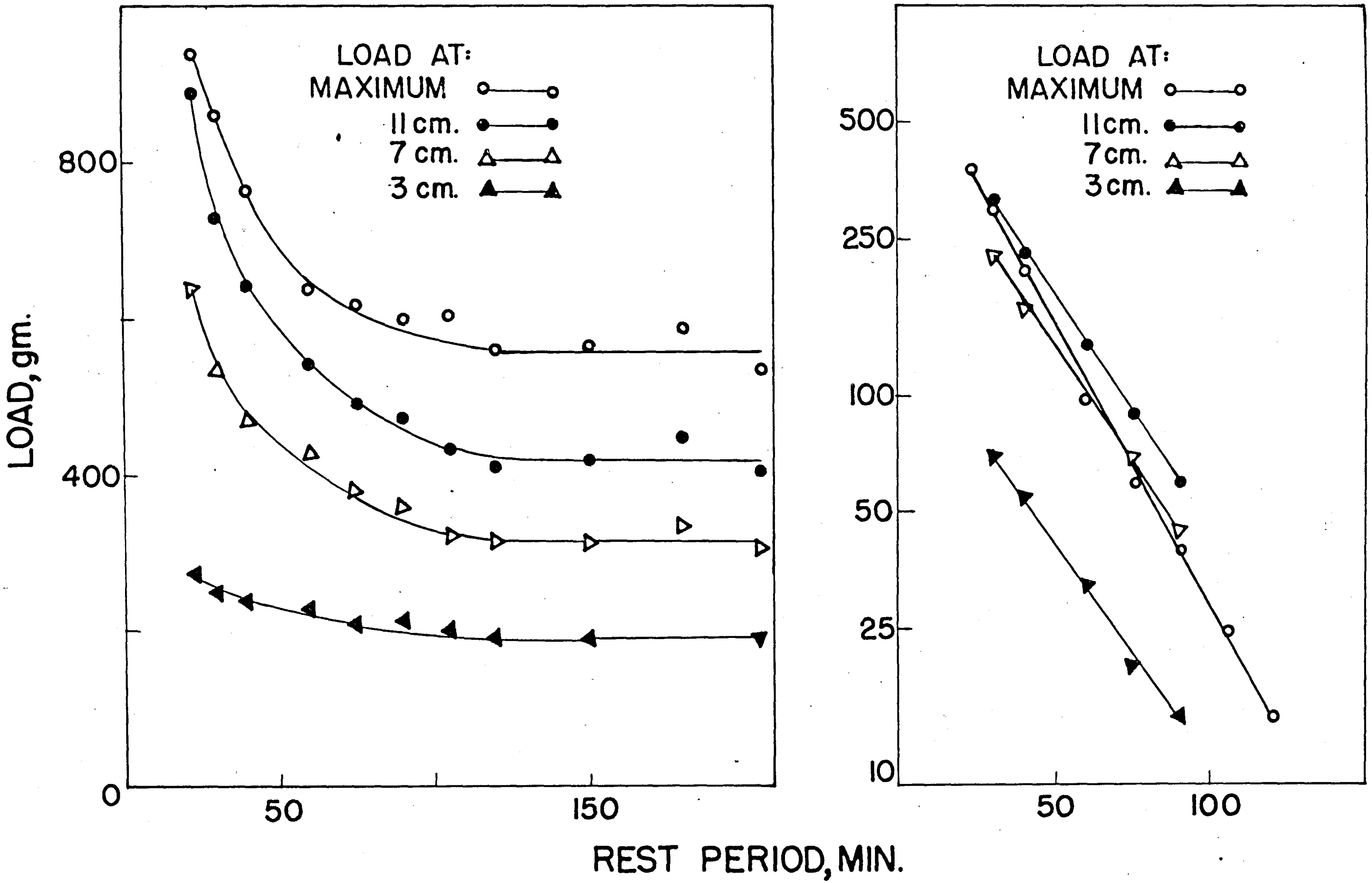


Fig. 11.

A

Curves showing the effect of elongation on the relaxation of load supported by bromated doughs.

B

Curves showing the effect of elongation on the exponential decay of load supported by bromated doughs.

Table VIII where the slopes of the logarithmic plots are recorded). The load at the maximum of the extensograms also gave a linear log. plot, but this was not parallel to the other three curves; this was generally found to be true in similar analyses of other relaxation experiments.

TABLE VIII

THE EFFECT OF ELONGATION ON THE FINAL LOAD VALUE AND THE SLOPE OF THE LOGARITHMIC PLOT OF RELAXATION DATA

Load read at	Final load value gm.	Slope of log plot
Maximum	560	-0.0147
11 cm.	415	-0.0107
7 cm.	310	-0.0118
3 cm.	190	-0.0112

The analysis of extensograms, using the load at the curve maximum, does not seem to yield the same information about the behavior of dough in the extensograph test as does the analysis using the load at a constant sample deformation. However, the latter would seem to be preferred as a basis for the analysis of extensograms since the information obtained about the behavior of dough in the extensograph test is essentially the same regardless of the particular value of constant sample deformation.

The Effect on the Relaxation of Bromated Doughs of Varying the Amount of Work When Shaping

It was reported in a previous section that work must be done on bromated doughs, by rounding them and rolling them into cylindrical shape after a reaction time had been allowed, for the bromate effect to be evident in subsequent dough-testing on the extensograph. A few experiments were made to determine whether a variation in the amount of work done in rounding and rolling the dough would affect the magnitude of the bromate effect as assessed by the extensograph.

Bromate-treated doughs were subjected to a two-fold variation in the amount of work done on the dough after a reaction time of two hours. The doughs were mixed from flour Sample D and contained 3 mgm. per cent bromate. At the end of the two hour reaction time, they were shaped on the extensograph, in which process the amount of work done on the dough was varied in two ways:

(a) some doughs were subjected to the normal amount of work on the extensograph by rounding each sample 20 times and rolling it once,

(b) some doughs were subjected to one-half the normal amount of work on the extensograph by rounding each sample 10 times and rolling it once.

Immediately after shaping, the two sets of doughs were subjected to a relaxation test in which increasing rest periods, varying from 10 to 180 minutes, were permitted before the dough was stretched on the extensograph. The data are recorded in Table IX and plotted in figure 12.

The curves of figure 12 show that a two-fold variation in the amount of work done on bromated dough samples, after a reaction time, did not greatly affect the rate of relaxation. However, they do suggest that a decrease in the amount of work done on bromated doughs does decrease slightly the final value of the load supported by the doughs.

TABLE IX

THE EFFECT OF VARYING THE WORK DONE IN SHAPING DOUGHS ON THE EXTENSOGRAPH ON THE SUBSEQUENT RELAXATION

Rest period min.	Load, gm., at 11 cm. extension	
	One-half normal work	Normal work
10	990	-
15	830	760
20	650	697
25	590	542
35	480	503
45	428	432
60	400	403
75	370	377
100	380	377
125	342	337
150	335	360
175	-	355
200	335	360

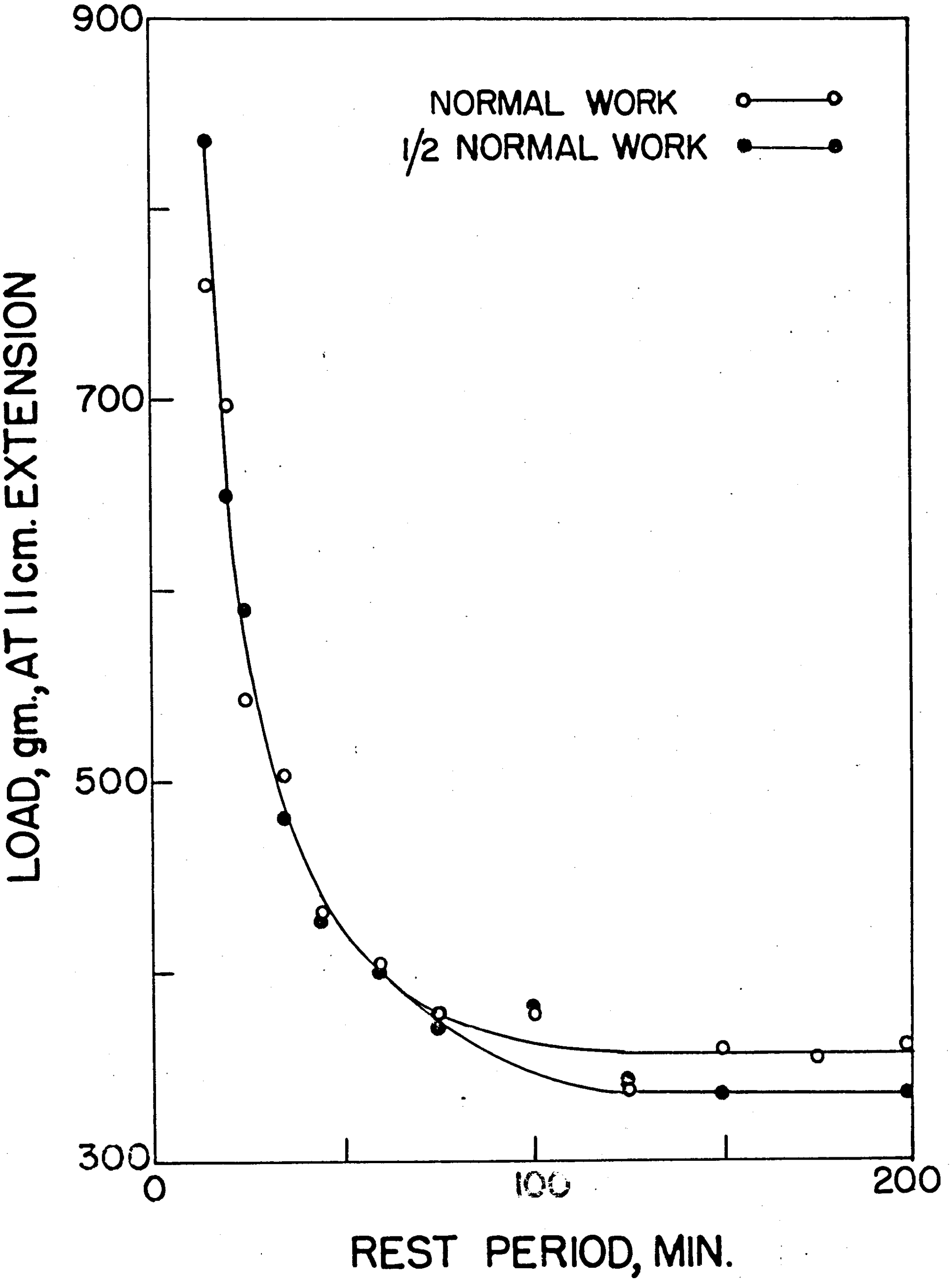


Fig. 12.

Curves showing the effect on relaxation of varying the work done in shaping doughs.

The Effect of Mixing in Nitrogen on the Relaxation of Untreated and Bromated Doughs

All the previous experiments were made by mixing the doughs in an atmosphere of air. Since Baker and Mize (5) have shown that oxygen incorporated into dough affects its physical properties, and since mixing a dough in air must cause incorporation of some oxygen, the effect of bromate on the physical properties of doughs mixed in air might be due to the presence of both bromate and oxygen. Relaxation experiments were therefore made on bromated doughs which had been mixed in an atmosphere of nitrogen in an effort to determine whether bromate, of itself, had an effect.

The technique employed in experiments in which doughs were mixed in atmospheres other than air has been described previously. Flour Sample D was used for these experiments on the effect of bromate on doughs mixed in nitrogen. Experiments were conducted by mixing control doughs and doughs containing 5 mgm. per cent potassium bromate for three minutes in an atmosphere of nitrogen, Doughs were allowed reaction times of 0, 1, and 2 hours. At the end of a given reaction time, dough samples were shaped on the extensograph and then tested after increasing rest periods. The data are recorded in Table X and plotted in figure 13.

The relaxation curves for the untreated and bromated doughs mixed in nitrogen were very similar to those of figures 7 and 8 for untreated and bromated doughs mixed in air. For the untreated control doughs mixed in nitrogen, the load decreased at the same rate with increasing rest period regardless of the reaction time between mixing

TABLE X

THE EFFECT OF REACTION TIME ON THE RELAXATION OF UNTREATED AND BROMATED DOUGHS MIXED IN NITROGEN

Rest period min.	Load, gm., at 11 cm. extension					
	Untreated doughs			5 mgm. % bromated doughs		
	Reaction time, hr.			Reaction time, hr.		
	0	1	2	0	1	2
5	675	530	505	720	-	-
10	420	330	305	430	770	-
15	310	275	255	335	-	-
20	-	-	-	290	470	-
25	-	220	210	-	-	-
30	230	-	-	250	397	690
40	205	200	-	-	-	-
45	-	-	185	265	315	580
50	205	-	-	-	-	-
60	210	170	180	210	310	520
75	190	-	-	240	-	490
80	-	165	-	-	285	-
90	-	-	-	-	-	445
100	190	170	-	255	290	-
120	-	-	-	-	-	395
125	180	-	-	245	290	-
150	-	-	-	250	-	390
175	-	-	-	252	-	350
200	-	-	-	-	-	350

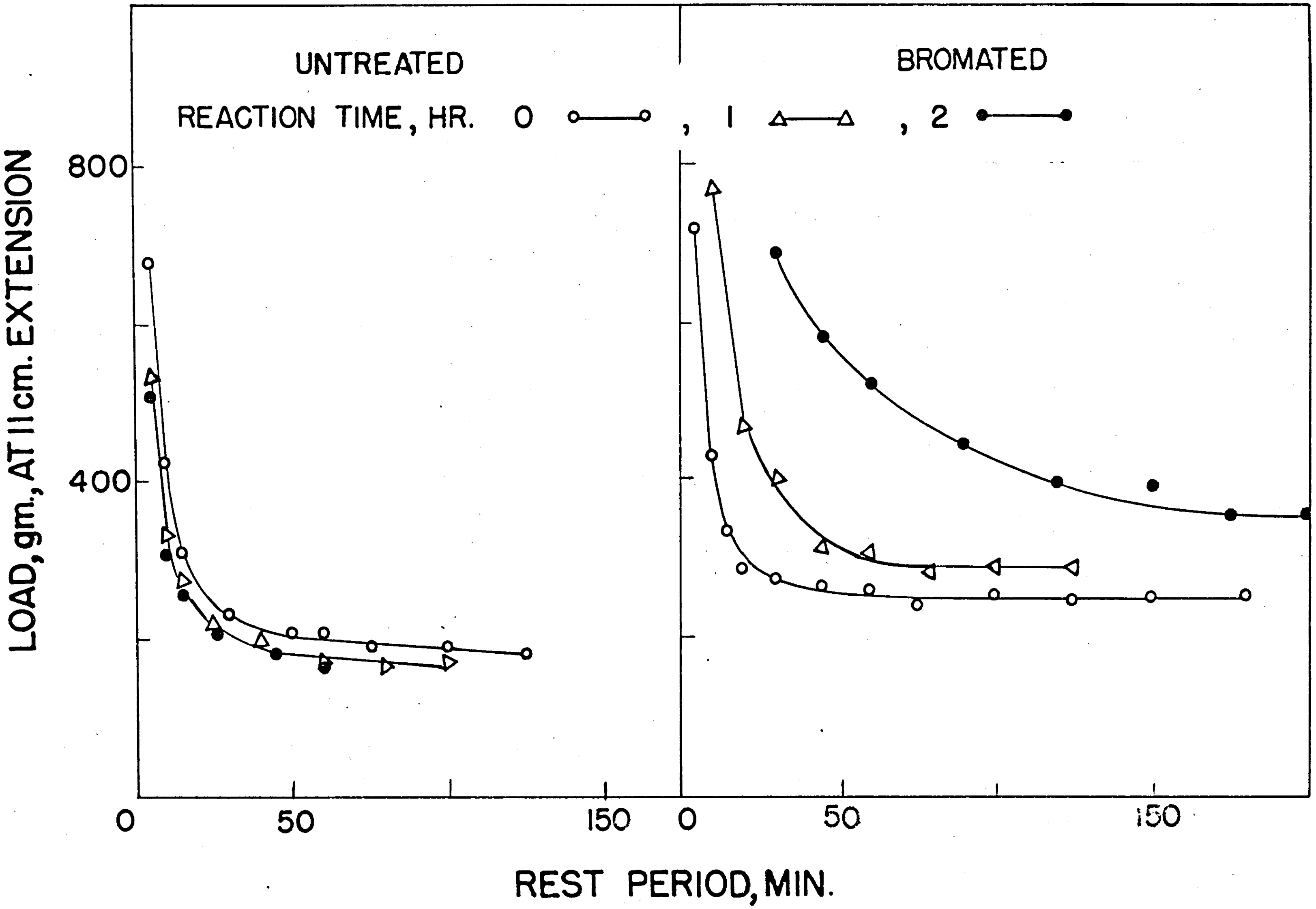


Fig. 13.

Curves showing the effect of reaction time on the relaxation of untreated and bromate-treated doughs mixed in nitrogen.

and shaping. As before, a linear decrease of load with rest period succeeded the exponential decrease. It is interesting to note that the slope of this linear portion of the load-rest period curve was the same for untreated doughs mixed in nitrogen and mixed in air, but was some 40 gm. higher for the doughs mixed in air at any given rest period.

For the 5 mgm. per cent bromated doughs mixed in nitrogen, the rate at which the load decreased, with increasing rest period, was less the longer the reaction time allowed. In addition, the longer the reaction time between mixing and shaping the bromated doughs, the higher was the value of the load at which the decay curve levelled off.

It is clear from the results as a whole that bromate does have an effect on the physical properties of a dough quite independently of the presence of oxygen.

The Effect of Mixing in Oxygen on the Relaxation of Untreated Doughs

With fermenting doughs, Baker and Mize (5) observed that the presence of bromate in vacuum- and nitrogen-mixed doughs resulted in characteristics similar to those of oxygen-mixed doughs. With this in mind, relaxation experiments were conducted on untreated doughs which had been mixed in an atmosphere of oxygen to determine whether the effects of bromate and oxygen were also similar in the absence of fermentation.

Flour Sample F was used for these experiments. Prior to use the flour samples were equilibrated in an atmosphere of oxygen using the procedure previously described. Four series of doughs were mixed in oxygen for three minutes and allowed reaction times of 0, 1, 2, and

3 hours. At the end of a particular reaction time, the doughs were shaped on the extensograph and then allowed increasing rest periods before being stretched. The data are recorded in Table XI and plotted in figure 14.

TABLE XI

THE EFFECT OF REACTION TIME ON THE RELAXATION OF DOUGHS MIXED IN OXYGEN

Rest period min.	Load, gm., at 11 cm. extension			
	Reaction time, hr.			
	0	1	2	3
10	740	-	-	-
20	590	940	-	-
30	465	740	-	-
40	-	710	897	-
45	412	-	-	910
50	-	612	710	-
60	425	590	660	790
70	-	-	590	-
75	445	550	-	750
80	-	-	635	-
90	393	525	-	705
95	-	-	610	-
110	430	480	560	625
130	-	485	550	600
135	430	-	-	-
150	-	455	510	580
160	422	-	-	-
175	-	-	550	610
180	-	470	-	-
190	440	-	-	-
200	-	460	510	543
225	420	-	540	562
250	-	-	508	500
275	-	-	-	550

It appears, from the curves of figure 14, that oxygen incorporated into dough produced effects which are somewhat similar to those produced by bromate. The rate at which the extensogram load decreased,

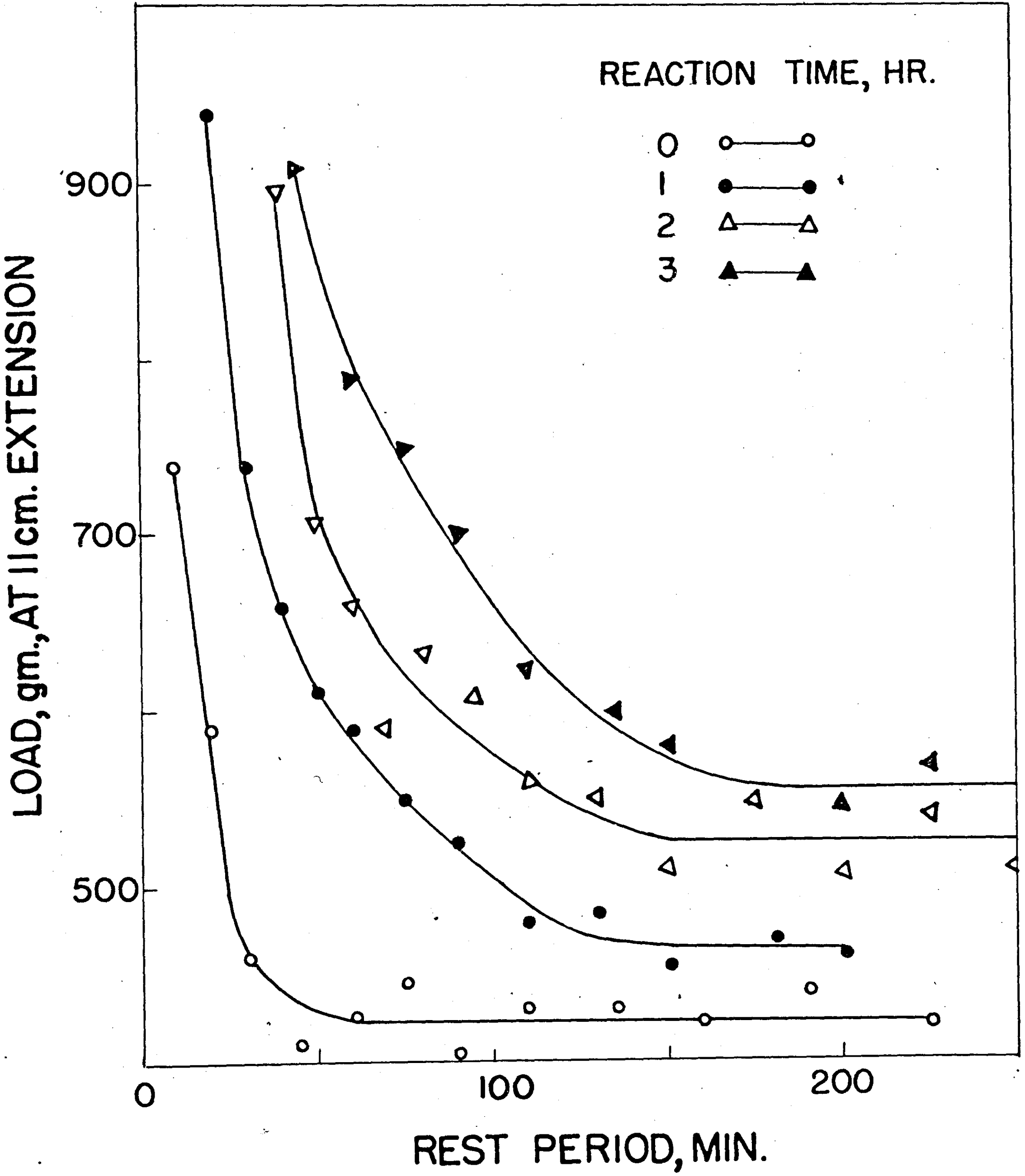


Fig. 14.

Curves showing the effect of reaction time on the relaxation of doughs mixed in oxygen.

with increasing rest period, for doughs given reaction times of 1, 2, and 3 hours, is slower than the rate when no reaction time was allowed. However, there appeared to be very little change in the rate of decrease of load with rest period as the reaction time was increased from 1 to 3 hours. This behavior is different from that of bromate in dough, where increasing reaction time produced considerable change in the rate of decrease of load. For oxygen-mixed doughs which had been allowed increasing reaction times, the extensogram load decayed to a stable value which was higher the longer the reaction time. These final load values are recorded in Table XII.

TABLE XII

THE EFFECT OF REACTION TIME ON THE FINAL LOAD SUPPORTED BY OXYGEN-MIXED DOUGHS

Reaction time hr.	Final load, gm., at 11 cm. extension
0	425
1	465
2	525
3	560

The Effect of Temperature and Reaction Time on the Relaxation of Bromate-treated Doughs

An experiment was made to determine the effect of temperature on the changes produced by bromate, with increasing reaction time, in the physical properties of flour doughs. For this experiment, flour Sample E and a bromate concentration of 3 mgm. per cent were used. The relaxation of the load supported by the bromate-treated doughs, with increasing rest period after shaping, was investigated for three different reaction times of 0, 2, and 4 hours at each of three different temperatures, 22.4°C, 30°C, and 35°C. All doughs, regardless of temperature, were mixed to the same absorption which was determined using the farinograph at 30°C. Doughs were mixed, using flour and solutions appropriately temperature-conditioned, to the required temperature and were stored at that temperature and at a high humidity for the desired reaction time. They were then shaped on the extensograph and allowed increasing rest periods at the desired temperature before being stretched. The data are recorded in Table XIII and plotted in figures 15, 16, and 17 to show the effect of reaction time on the relaxation of the bromated doughs at each temperature.

In these experiments, the extensograph was operated at a temperature of 30°C. This was essential, in order that the viscosity of the damping liquid (see figure 3, where the damping unit is shown at 9) be unchanged, and the action of the extensograph remain the same regardless of the temperature of the doughs being tested.

The curves of figures 15, 16, and 17 illustrate, again, the progressive changes produced by bromate with increasing reaction time in the extensograph properties of flour doughs. The effect of increasing reaction time at each temperature was to bring about a decrease in the rate at which the load supported by bromated doughs changed with increasing rest period after shaping. The load supported by the doughs, under these different conditions of temperature and reaction time, decreased to a final stable value except for the experiment at 35°C with a 4 hour reaction time. These doughs probably also would have reached

TABLE XIII

THE EFFECT OF TEMPERATURE AND REACTION TIME ON THE RELAXATION OF 3 mgm. PER CENT BROMATE-TREATED DOUGHS

Rest period min.	Load, gm., at 11 cm. extension								
	22.4°C			30°C			35°C		
	Reaction time, hr.			Reaction time, hr.			Reaction time, hr.		
	0	2	4	0	2	4	0	2	4
5	-	-	-	865	-	-	870	-	-
10	873	-	-	620	885	-	540	-	-
15	635	910	-	483	770	-	430	785	-
20	537	713	-	443	675	-	385	635	-
22.5	-	-	887	-	-	-	-	-	-
25	-	680	-	-	575	885	-	600	-
30	438	570	735	380	505	-	360	490	-
35	-	-	-	-	-	765	-	-	-
40	444	500	645	-	-	-	-	470	-
45	-	-	-	363	455	670	325	-	-
50	392	512	-	-	-	-	-	430	-
60	390	470	548	340	392	603	310	405	610
75	386	460	495	335	360	523	300	362	550
90	386	410	475	332	358	480	292	370	585
105	-	-	435	-	-	-	-	-	535
120	360	408	412	330	345	-	290	350	533
125	-	-	-	-	-	394	-	-	-
145	-	-	-	-	-	-	-	-	540
150	368	415	420	315	343	460	295	322	-
170	-	-	-	-	-	-	-	-	490
175	-	-	-	-	-	400	-	-	-
180	355	400	450	330	340	-	300	325	-
200	-	-	-	-	-	428	-	-	487
205	-	-	405	-	-	-	-	-	-
225	-	-	-	-	-	445	-	-	-

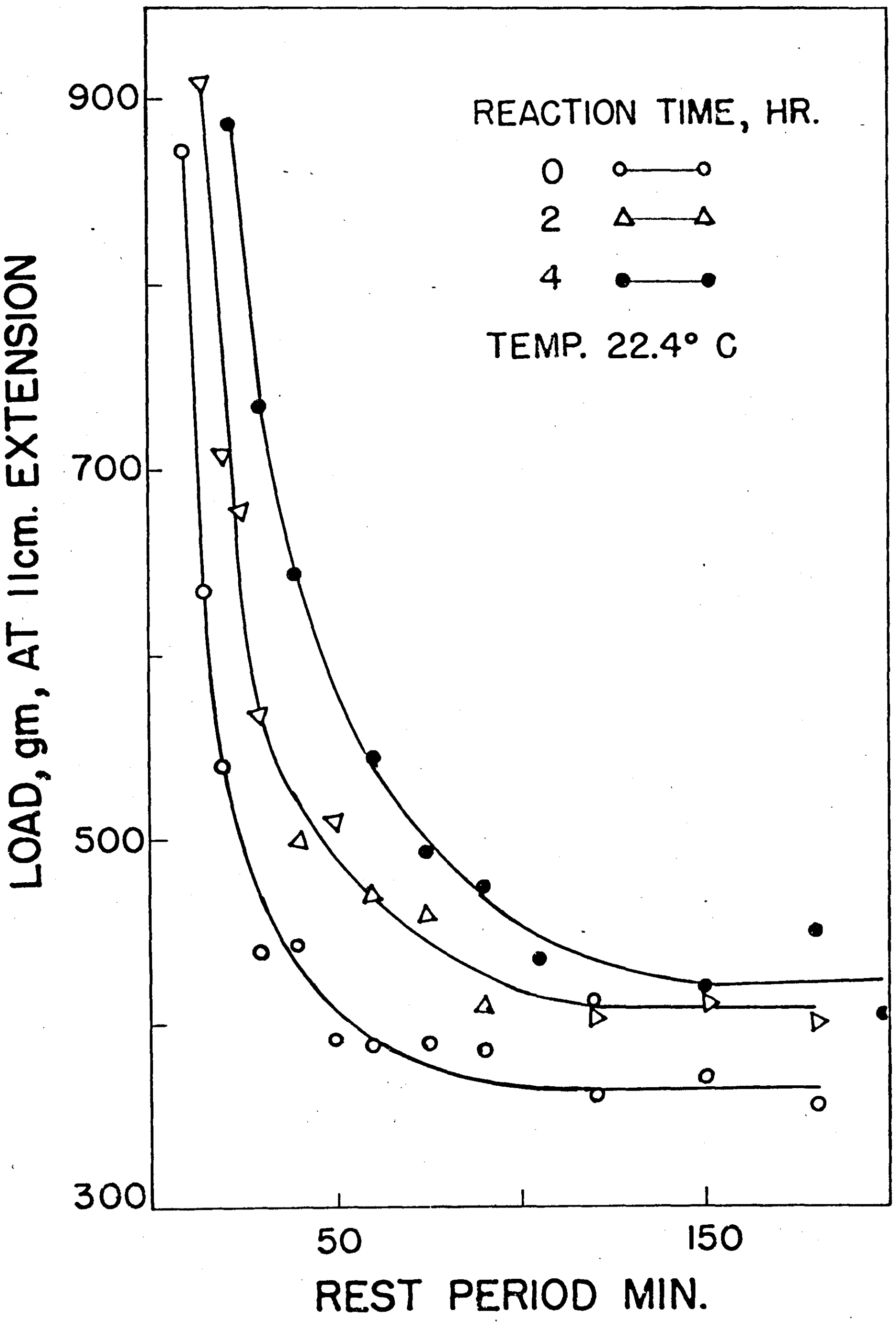


Fig. 15.

Curves showing the effect of reaction time on the relaxation of bromated doughs at a temperature of 22.4°C.

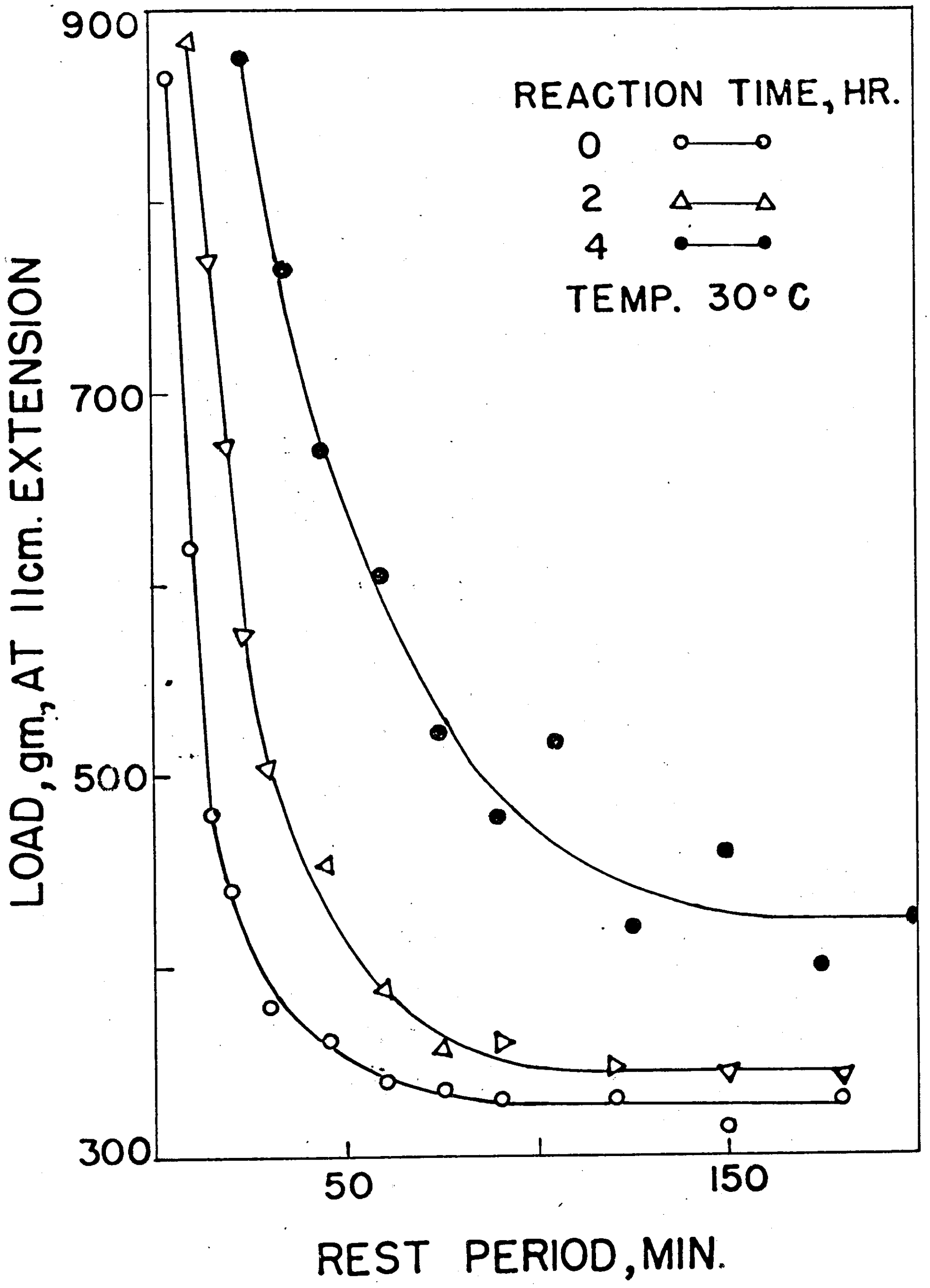


Fig. 16.

Curves showing the effect of reaction time on the relaxation of bromated doughs at a temperature of 30°C.

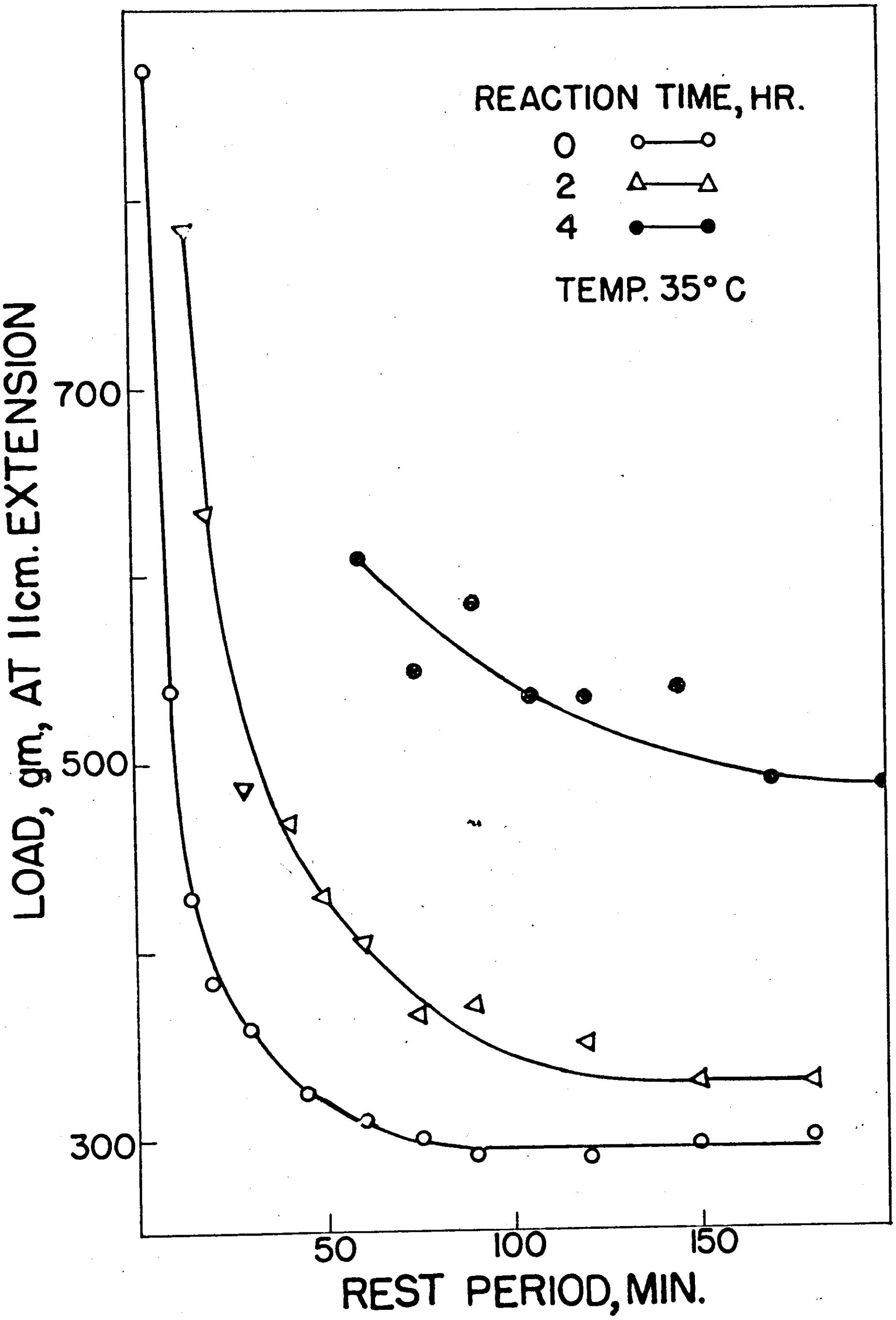


Fig. 17.

Curves showing the effect of reaction time on the relaxation of bromated doughs at a temperature of 35°C a stable value had longer rest periods been permitted. The final load values for each reaction time at each of the three temperatures are recorded in Table XIV.

TABLE XIV

THE EFFECT OF TEMPERATURE AND REACTION TIME ON THE FINAL LOAD SUPPORTED BY BROMATED DOUGHS IN RELAXATION EXPERIMENTS

Reaction time hr.	Final load, gm., at 11 cm. extension Temperature, °C. 22.4	30	35
0	365	325	295
2	405	350	330
4	420	430	-

The data of Table XIV, and the corresponding figures, show that for a given reaction time, the final value of the load was decreased by an increase of temperature. There is also a suggestion that the final load increased more rapidly, with increasing reaction time, the higher the temperature. The curves also reveal that the rate of relaxation of extensogram load changed more rapidly, with increasing reaction time, with an increase of temperature. Qualitatively then, the reaction of potassium bromate in flour dough, as indicated by changes in physical extensograph properties, appears to be accelerated by an increase in temperature.

The relaxation curves of figures 15, 16, and 17 illustrate again the important features of the bromate reaction in flour dough. The reaction of bromate is highly time-dependent, and the bromate reaction is not apparent until work has been done upon the dough.

The Effect of Varying Mixing Time on the Extensograph Properties of Doughs Mixed in Nitrogen, Air, and Oxygen

Some interesting and informative experiments were made in which flour doughs were mixed from flour Sample D for various periods of time, from 1 to 8 minutes, in each of the atmospheres nitrogen, air, and oxygen. Immediately after mixing, these doughs were allowed a reaction time of one hour, after which they were shaped on the extensograph and then given a rest period of 45 minutes before being stretched. The data are recorded in Table XV and shown graphically in figure 18 where load is plotted against mixing time.

TABLE XV

THE EFFECT OF VARYING MIXING TIME IN NITROGEN, AIR, AND OXYGEN ON DOUGH PROPERTIES AS DETERMINED FROM 45-MINUTE EXTENSOGRAMS

Mixing time min.	Load, gm., at 11 cm. extension		
	Dough mixed in		
	Nitrogen	Air	Oxygen
1	212	240	492
2	205	235	495
4	210	268	587
6	210	372	680
8	228	423	802

Variation of mixing time in nitrogen produced virtually no change in the load supported by the doughs with increasing mixing time, but when doughs were mixed in air a different behavior was observed. No change in the load supported by doughs mixed in air occurred as mixing time was increased from 1 to 2 minutes although the load was about 25 gm. greater than for doughs mixed in nitrogen. As the mixing time in air was increased beyond 2 minutes, a progressive and apparently

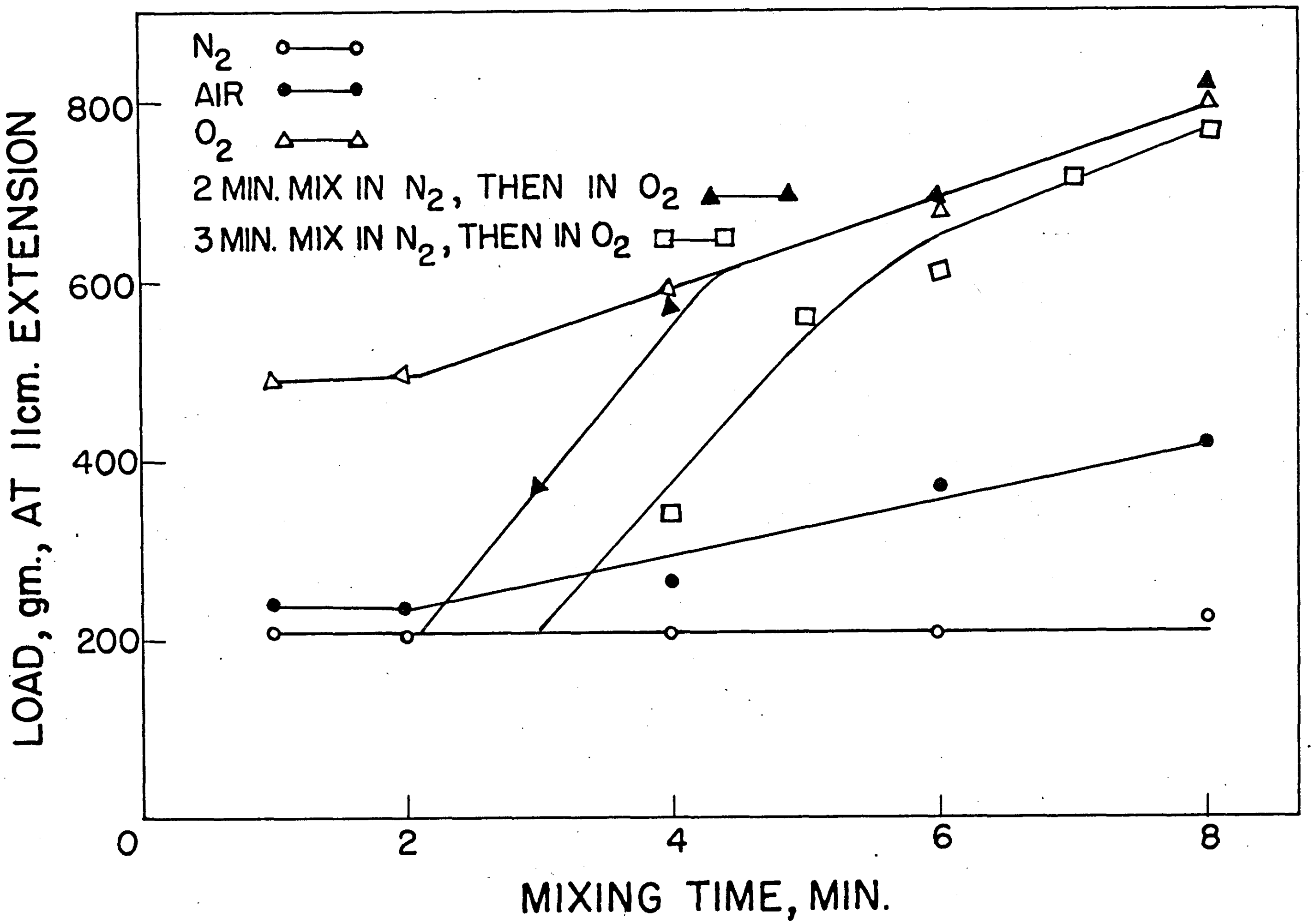


Fig. 18.

Curves showing the effect of varying the mixing time in nitrogen, air, and oxygen on extensograph dough properties.

linear increase in load was observed. A similar change in load with increasing mixing time occurred when mixing was conducted in oxygen. The constant load supported by doughs mixed in oxygen, as the mixing time was increased from 1 to 2 minutes, was about 280 gm. higher than it was for the nitrogen-mixed doughs.

These results show that oxygen, incorporated into doughs, has an appreciable effect on dough properties. The results suggested that oxygen itself, or oxygen together with the mixing action, might be the limiting factor in the changes that occur in dough properties with increased mixing time. In an attempt to obtain information on this point, the following experiments were made. Doughs were mixed for increasing periods of time, the initial two minutes of mixing being conducted in an atmosphere of nitrogen and the remainder of the mixing in oxygen. A similar experiment was made by mixing for an initial period of three minutes in nitrogen, followed by mixing in oxygen. The doughs were allowed a reaction time of 1 hour, shaped, and then stretched 45 minutes later. The data are recorded in Table XVI and are plotted, along with the previous data for various mixing times, in figure 18.

The curves in figure 18 showing the effect on dough properties of increased mixing time in oxygen for doughs given an initial mix in nitrogen, do not seem to provide an answer to the problem of whether the effect of oxygen in dough, with increased mixing time, is due only to the oxygen concentration or due to oxygen plus some effect of mixing. When the atmosphere in which the doughs were mixed was changed from nitrogen to oxygen, the extensogram load increased rapidly with further mixing from the constant value for mixing in nitrogen. The initial rate of increase of load with mixing time in oxygen appeared to be independent of the pre-mixing time in nitrogen. The load increased at a steady rate with mixing time in oxygen until it approached values attained when mixing was conducted throughout in oxygen.

TABLE XVI

THE EFFECT OF VARYING MIXING TIME IN OXYGEN ON EXTENSOGRAPH PROPERTIES OF DOUGHS GIVEN AN INITIAL MIX IN NITROGEN

Mixing time min.	Distribution of mixing time min. in N_2	min. in O_2	Load, gm., at 11 cm. extension
3	2	1	375
4	2	2	580
6	2	4	690
8	2	6	820
4	3	1	340
5	3	2	562
6	3	3	610
7	3	4	715
8	3	5	768

Some experiments were made in which mixing times in excess of 8 minutes were used. However, when doughs were mixed for such long periods of time, they became very sticky. Doughs mixed for 10 minutes were so sticky as to make it impossible to handle them in the usual manner. For this reason, data for mixing times in excess of 8 minutes have not been included in Table XV and XVI. Such trials did suggest, however, that the linear increase of load with mixing time in oxygen did not continue indefinitely. Rather, the doughs seemed to reach a maximum in the load in the neighborhood of 8 minutes mixing, and further increase of mixing time in oxygen brought about a decline in the load. This behavior did not appear to be shown for mixing times in excess of 8 minutes in air, where it appeared that the linearity of the load-mixing time plot was continued up to mixing times of 12 minutes.

The extensograms obtained with doughs mixed in air for increased periods of time showed a progressive increase of load and coincidentally a progressive decrease in the extent to which the dough could be stretched before breaking. The extensograms obtained on the nitrogen-mixed doughs with increased mixing time showed a progressive decrease in extensibility but supported an almost constant load. The effect of increased mixing time on the extensogram dimensions of doughs mixed in nitrogen and in air is shown by the data in Table XVII. In this Table is recorded the dough extensibility, or total length in extensogram cm. to which a dough was stretched when it broke. The extensibility can be translated into an actual dough length, but for purposes of comparison this need not be done.

TABLE XVII

THE EFFECT OF MIXING TIME ON EXTENSOGRAM DIMENSIONS OF DOUGHS MIXED IN NITROGEN AND IN AIR

Mixing time min.	Nitrogen-mixed doughs		Air-mixed doughs	
	Load, gm., at 11 cm.	Extensibility cm.	Load, gm., at 11 cm.	Extensibility cm.
1	212	23.0	240	23.5
2	205	23.5	235	23.0
4	210	21.5	268	21.5
8	228	19.0	423	17.7
12	270	16.5	562	15.5

The data of Table XVII indicate that the decrease in extensibility with increasing mixing time is almost parallel for both the nitrogen- and the air-mixed doughs. The observed progressive decrease of extensibility of nitrogen-mixed doughs with mixing time is, indeed, interesting. Previous experience with extensograms had always shown that a decrease in extensibility was coincident with an increase in the load supported by the dough. However, these data on nitrogen-mixed doughs suggest that these two extensogram dough properties, load and extensibility, are not necessarily related. In these particular experiments, the increased load with mixing time seems to be associated with the successive incorporation of oxygen into the doughs. On the other hand, the decreased extensibility of the doughs seems to be associated with the amount of mixing that the doughs received.

The Effect of Varying Mixing Time and Bromate Concentration on the Extensograph Properties of Doughs Mixed in Nitrogen, Air, and Oxygen

The experimental extensograph technique described in the previous section was used to investigate the effect of varying mixing time on the bromate reaction in doughs mixed in each of nitrogen, air, and oxygen. Doughs containing 0, 1, 2, 3, 4, 5, and 6 mgm. per cent potassium bromate were mixed, for various times of from 1 to 8 minutes, using flour Sample D. After mixing, each dough was allowed a reaction time of one hour, shaped on the extensograph, and then stretched 45 minutes later. The data are recorded in Table XVIII and plotted in figure 19.

The curves of figure 19 show that the addition of successive increments of bromate produced a linear increase in the load supported

TABLE XVIII

THE EFFECT OF VARYING MIXING TIME AND BROMATE CONCENTRATION ON THE EXTENSOGRAPH PROPERTIES OF DOUGHS MIXED IN NITROGEN, AIR, AND OXYGEN

Bromate concentration mgm. %	Load, gm., at 11 cm. extension			
	Mixing time, min.			
	1	2	4	8
	Nitrogen-mixed doughs			
0	216	205	-	229
1	246	222	215	241
2	270	245	245	297
3	307	268	281	345
4	326	304	301	365
5	337	341	358	460
6	380	392	400	517
	Air-mixed doughs			
0	240	232	277	425
1	259	245	290	456
2	280	282	317	507
3	286	309	330	522
4	329	337	350	545
5	358	380	378	574
6	398	421	442	601
	Oxygen-mixed doughs			
0	492	495	587	802
1	481	555	640	-
2	485	557	702	-
3	505	602	665	-
4	581	635	687	-
5	603	665	765	-
6	615	730	825	-

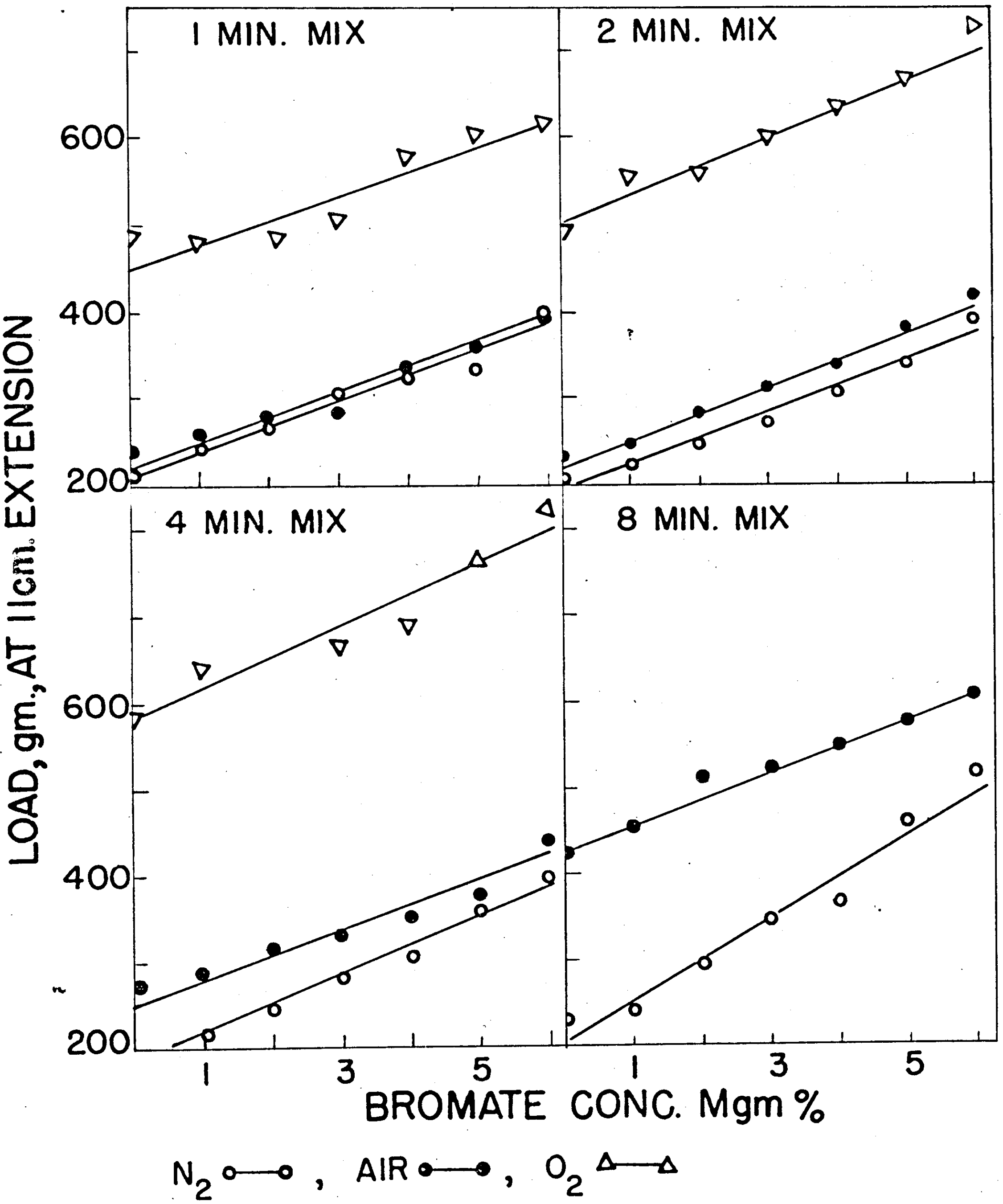


Fig. 19.

Curves showing the effect of varying mixing time and bromate concentration on extensograph properties of doughs mixed in nitrogen, air, and oxygen.

by the doughs, regardless of mixing time, in each of the atmospheres, nitrogen, air, and oxygen. The slope of the load-bromate concentration plot was nearly the same for mixing times of 1, 2, and 4 minutes in nitrogen. Since each of these three curves starts from nearly the same origin, it may be concluded that the effect of bromate in dough was independent of the mixing time in the range studied.

For a given mixing time in each of the gases, the load-bromate curves were almost parallel. This suggests that oxygen of the air and pure oxygen, when incorporated into dough, have an effect on dough properties which is superimposed on the effect of bromate. This effect of oxygen in dough is, in part, determined by the amount of mixing the dough has received. The amount of mixing is a measure of the amount of oxygen incorporated, as can be seen by comparing the load-bromate concentration curves for doughs mixed in nitrogen and in air at each of the different mixing times. As mixing time was increased, the curve for the air-mixed doughs was raised to successively higher levels above the curve for the nitrogen-mixed doughs.

An interesting observation with respect to the effect of oxygen in dough can be seen by referring to figure 19. It is apparent that mixing for 1 minute in oxygen and mixing for 8 minutes in air gave results which, in terms of the extensogram load supported by the doughs, were almost equivalent across the range of bromate concentrations. If the oxygen effect depended solely upon the amount of oxygen incorporated into the dough during mixing, it would be expected that 1 minute mixing in oxygen would be equivalent to 5 minutes mixing in air. This aspect, however, has not been further investigated.

The Effect of the Cupric Ion on the Extensograph Properties of Doughs

Many chemical reagents are known to be able to produce changes in the physical properties of flour doughs. It was thought that the incorporation of the cupric ion into doughs and the study of the resulting changes in physical extensograph properties might be of some help in interpreting the chemistry of the changes in dough structure produced by potassium bromate. Copper is renowned for complex compound formation with ammonia and amino acids (74).

A preliminary experiment on the effect of the copper ion on the physical extensograph dough properties suggested that copper had an immediate effect as well as an effect which increases with reaction time. To investigate this in more detail, the following experiments were made using flour Sample F. Several series of doughs were mixed, each series containing a different amount of cupric chloride ranging from 1 to 4 mgm. per cent. Doughs of a given copper concentration were set aside immediately after mixing and each was allowed a reaction time ranging from 0 to 4 hours. At the end of a given reaction time, the dough was shaped and then stretched 45 minutes later. The load supported by the various doughs was read from the extensograms in the usual way. The data are recorded in Table XIX and plotted in figure 20.

Copper had an immediate effect on dough properties as indicated by the fact that these curves did not have a common origin for zero reaction time. For each concentration of copper, the extensogram load increased quite rapidly with increasing reaction time up to about 1 hour, when a maximum in this property was reached. This maximum appeared to be maintained with increasing reaction time up to 4 hours.

TABLE XIX

THE EFFECT OF INCREASING REACTION TIME ON THE PROPERTIES OF COPPER-TREATED DOUGHS AS DETERMINED FROM 45-MINUTE EXTENSOGRAMS

Reaction time min.	Load, gm., at 11 cm. extension			
	Cupric chloride concentration, mgm. %			
	1	2	3	4
0	400	510	648	710
5	-	585	733	-
10	-	615	805	-
15	-	635	812	965
30	435	650	870	-
45	-	710	942	-
60	460	720	970	-
120	425	690	945	-
180	415	690	970	-
240	435	-	940	-

For the range of copper concentrations employed, the copper content of the dough appeared to be the limiting factor in the changes which occurred in the dough properties, as indicated by the linear increase of load with copper concentration when no reaction time was allowed (Table XX).

TABLE XX

THE EFFECT OF COPPER CONCENTRATION ON THE EXTENSOGRAM PROPERTIES OF DOUGHS ALLOWED NO REACTION TIME

Cupric chloride concentration, mgm. %	Load, gm., at 11 cm. extension
0	290
1	400
2	510
3	648
4	710
5	790

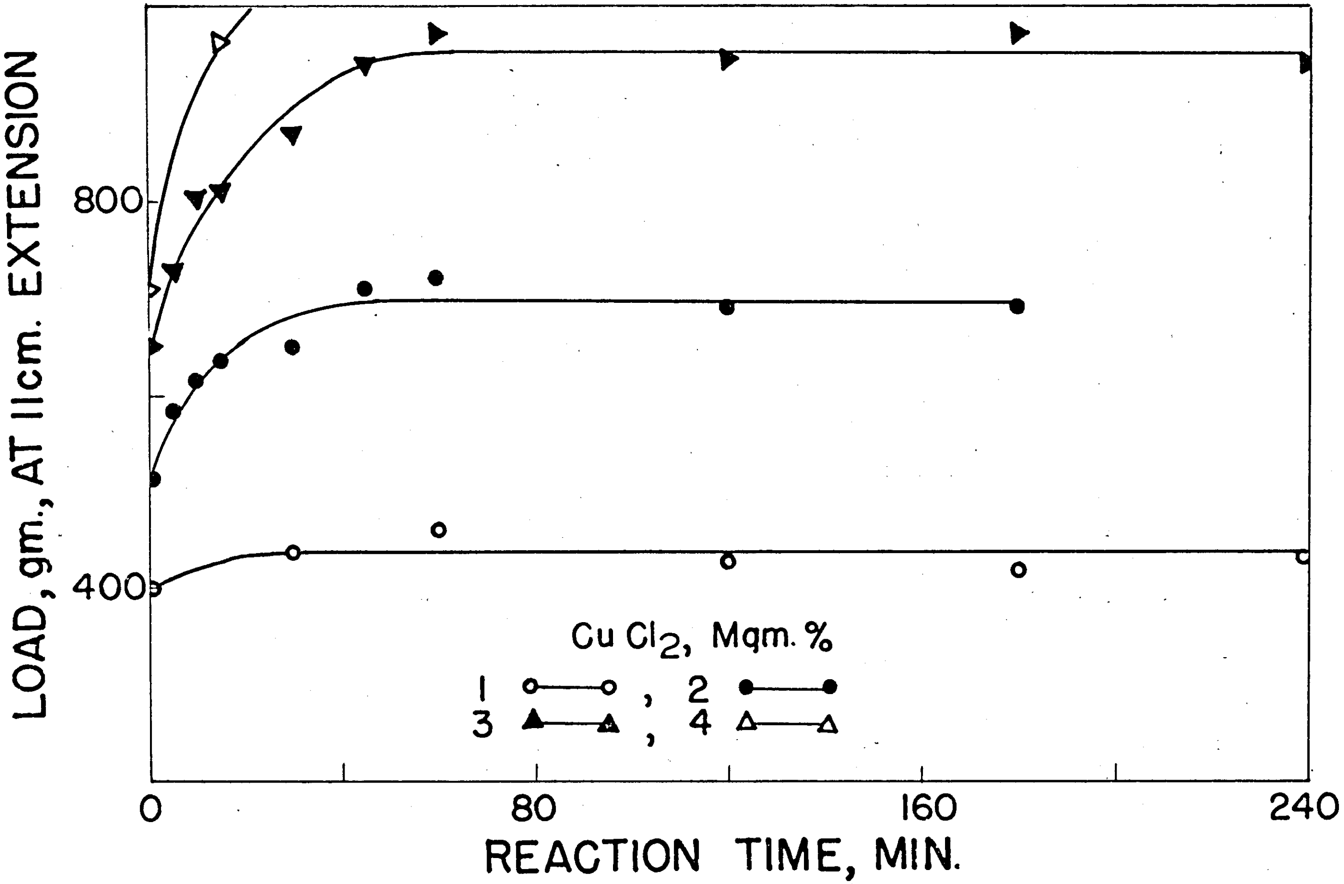


Fig. 20.

Curves showing the effect of reaction time on the extensograph properties of doughs containing cupric chloride.

A further indication that the copper concentration was the limiting factor in the changes which occurred in dough properties was the linear relation between the copper content of a dough and the final maximum value of load attained with increasing reaction time, e.g.

$CuCl_2$ concentration, mgm. per cent	1	2	3
Final load, gm.	430	690	955

Some experiments were made to determine the effect of the copper ion, with increasing reaction time, on the relaxation of the load supported by such doughs as the rest period was increased between shaping and stretching. Doughs containing 2 mgm. per cent and 4 mgm. per cent cupric chloride, as well as untreated doughs, were prepared using flour Sample E. The doughs were allowed reaction times of 0, 1, and 2 hours, shaped at the end of a particular reaction time, and then allowed increasing rest periods before being stretched. The results are recorded in Table XXI and plotted in figure 21.

The relaxation curves of figure 21 for the untreated control doughs indicate that the load relaxed at the same rate regardless of the reaction time allowed between the mixing and shaping operations. Doughs treated with 2 mgm. per cent copper and allowed reaction times of 1 and 2 hours appeared to have identical relaxation rates, which were considerably slower than that for doughs similarly treated but given no reaction time. This is taken to indicate that the reaction of the copper ion in the flour doughs is virtually completed in one hour's time since, for reaction times in excess of one hour, no further change in physical extensograph dough properties was observed.

TABLE XXI

THE EFFECT OF REACTION TIME ON THE RELAXATION OF CUPRIC CHLORIDE-TREATED DOUGHS

Rest period min.	Load, gm., at 11 cm. extension							
	Cupric chloride concentration, mgm. %							
	0			2			4	
	Reaction time, hr.			Reaction time, hr.			Reaction time, hr	
	0	1	2	0	1	2	0	1
5	955	812	840	-	-	-	-	-
10	600	505	590	-	-	-	-	-
15	-	410	-	805	-	-	-	-
20	385	-	360	-	1000	-	-	-
25	-	330	-	-	-	-	-	-
30	325	-	-	600	810	-	885	-
35	-	287	310	-	-	-	-	-
40	-	-	-	-	650	705	753	-
45	292	270	272	510	-	-	-	-
50	-	-	-	-	623	610	-	-
60	280	245	268	468	585	590	650	950
75	278	253	260	455	535	530	595	850
90	255	240	-	458	500	495	550	825
100	-	-	250	-	-	-	-	-
105	-	-	-	-	-	468	530	785
110	250	-	-	-	455	-	-	-
120	-	235	-	440	-	-	550	-
125	-	-	252	-	-	450	-	735
130	257	-	-	-	448	-	-	-
150	260	225	238	410	415	425	550	690
175	-	-	240	397	430	420	505	662
180	-	212	-	-	-	-	-	-
200	250	-	222	407	415	410	550	633
210	-	225	-	-	-	-	-	-
225	-	-	215	380	410	418	-	620
240	-	220	-	-	-	-	-	-
250	-	-	220	390	400	405	-	585
275	-	-	-	-	-	-	-	580
300	-	-	-	-	-	-	-	585

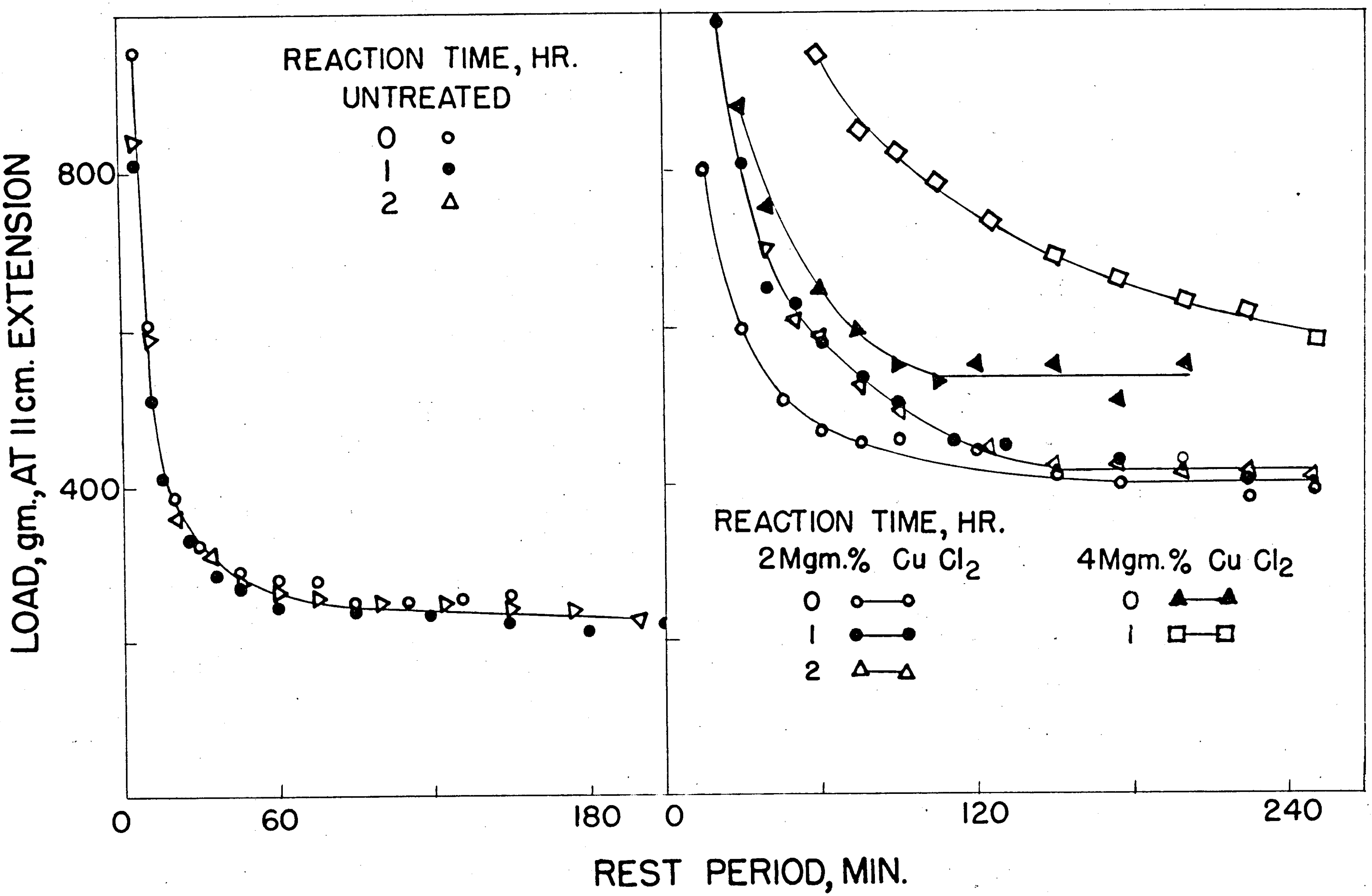


Fig. 21.

Curves showing the effect of reaction time on the relaxation of untreated and cupric chloride-treated doughs.

Relaxation occurred much more slowly in doughs treated with 4 mgm. per cent cupric chloride than in doughs treated with 2 mgm. per cent. The change in the rate of relaxation with increasing reaction time was much more pronounced with the higher copper concentration. Relaxation experiments indicated that the load, supported by cupric chloride-treated doughs, decayed to stable values which increased to a maximum with increasing reaction time.

The changes produced by copper in the physical properties of flour doughs are somewhat like those produced by the action of bromate. The changes produced by copper are time-dependent, but the reaction appears to have gone to completion in about one hour's time.

DISCUSSION

The fundamental properties responsible for the behavior of dough in the extensograph are elasticity and viscosity. Both of these properties are involved throughout most of the stretching process, hence the extensograph does not provide a measurement of either dough viscosity or modulus of elasticity individually. Similarly, it can be said that most of the physical dough testing instruments in use today are not capable of measuring fundamental physical properties. In general, the behavior of dough as revealed by such instruments involves a complex interaction of a number of basic physical properties, and physical testing of flour doughs as currently practiced is largely empirical. Although a vast amount of experimental data has been accumulated through the use of various physical dough-testing instruments, much of this information is interpretable only in terms of the particular machine and method used. This is because of the difficulty of definitely separating and identifying, from the empirical results yielded by the instrument, those physical properties which are of primary significance and the further difficulty of relating these properties to the actual structure of the material. However, some degree of success appears to be possible in analyzing the results of the present study and in making use of the analysis to deduce information about the chemistry responsible for the behavior of the material in the extensograph test.

The Extensograph Test

The physical properties that a material exhibits are dependent on its molecular structure. In flour dough, the protein or gluten forms an elastic network which dominates the mechanical behavior. There is little information available concerning the structure of gluten in flour dough, but a number of studies have been conducted on gluten which has been washed from dough, and these have yielded some information about the structure of the isolated gluten. Kuhlmann (46), as a result of solubility and swelling studies, concluded that gluten, considered as a natural high polymer, represented a complex of proteins forming micelles of various lengths. Ultracentrifuge techniques (70), applied to studies of gluten, have also led to a concept of micellar structure. McCalla and co-workers (50, 51), studied the behavior of gluten dispersed in sodium salicylate solution, and showed that a series of protein fractions could be precipitated from this solution by gradual addition of magnesium sulfate. The properties of these precipitated fractions varied continuously from one to another in contradiction to the classical concept of the existence of gliadin and glutenin as independent proteins in wheat gluten. These authors considered gluten to be a protein-lipid complex apparently formed when a dough is made. Their studies suggested that the properties of the complex, called gluten, were determined by much more complicated factors than the basic properties of the protein itself and that interactions between the protein and its environment, i.e. other flour and dough constituents, played a considerable part in determining the properties of the dough as a whole.

Schofield and Scott Blair (62) demonstrated that gluten is responsible for the mechanical behavior of dough. It is conceivable that, when dough is stretched or sheared, the polypeptide protein molecules tend to be uncoiled somewhat and possibly, to some extent, to assume a parallel arrangement. Such partial uncoiling and orientation of long chain molecules does occur in solutions subjected to shear action and is responsible for the phenomenon of birefringence. It is also widely recognized that a similar partial uncoiling and orientation may be present in the flow of molten polymers (64).

Some evidence for uncoiling and orientation of protein of flour dough has been presented by Halton and Scott Blair (31). These authors observed a fibrous structure, visible with the naked eye, in dough which had been extended until it broke. These fibres, which manifested themselves only when the dough was stretched, tended to slip past one another at high stresses and, at sufficiently high stress, progressive tearing of the fibres occurred until the dough was ruptured.

Further evidence for the concept that chain protein molecules in dough become partially aligned when subjected to shearing action is found in an observation by Schofield and Scott Blair (60) on fermenting dough systems. Dough samples, made up with yeast, were kneaded well, pulled out, i.e. stretched in one direction, and then folded over. This operation was repeated a number of times, the stretching and folding always being in the same direction in the dough. Subsequent expansion of the dough by carbon dioxide evolution during fermentation was uneven, the smaller expansion being in the direction in which the dough had previously been folded. It was postulated that the work done on the dough had uncoiled the protein chains and tended to align them in the direction of the stretch. When gas formed in the dough, expansion in this direction was more difficult because the chains were already stretched and aligned. Expansion in this direction could only take place if the aligned chains were to slide over one another, but this is hampered by reactive groups in neighboring chains which tended to bond together. Slippage in this direction could occur but only when such bonds break, and any bonds which did break would quickly reform as slip occurred. Expansion in the other direction was thought to involve a lateral displacement of the protein chains. Once the bonds between the reactive groups in neighboring chains were broken by displacement in this direction, there was not the same possibility of reformation as described above.

This type of behavior of the protein in dough, when subjected to shearing action, is of interest in connection with the changes produced in the properties of dough when rounded and rolled on the extensograph. When a dough was stretched on the extensograph soon after it had been rounded and rolled, it supported a very high load, but the load that a dough could support decreased rapidly as the rest period between shaping and stretching was increased. This rapid decrease of load with rest period for untreated doughs was more or less complete in about 45 minutes, and further increase of rest period in excess of 45 minutes resulted in little change of extensogram load.

This behavior may be attributed to the shaping operation, in which the dough is impaled on the pin in the rounder and subjected to a shearing action as the operation proceeds. In the process, the protein molecules of the dough must be disturbed rather drastically from their equilibrium positions in the resting dough, and in view of the type of shear, it is conceivable that an orientation of these molecules might result in much the same way as long chain molecules in solution become oriented when the solution is sheared between concentric cylinders.

It is postulated then, that when a dough is taken from the rounder, the molecules are more or less uncoiled and somewhat aligned. The dough is immediately put through the roller to obtain a test sample of the required dimensions. In the roller, the ball of dough is pressed between a revolving central cylinder and a concentric outer drum, and this operation also subjects the dough to a shearing action. Having gone through these two operations, a dough might be expected to have most of the long chain protein molecules disturbed from their equilibrium shapes in the resting dough.

If the protein molecules in the dough are partially uncoiled and oriented, a greater force should presumably be required to stretch the dough than would be required by a dough in which the molecules are coiled and oriented randomly. Thus, the uncoiling and orientation of the molecules in a dough as a result of the shaping operation could account for the extensogram obtained on a dough tested soon after being shaped. Such a dough does require a considerable force to stretch it. However, if time is allowed to elapse between shaping a dough and subsequently stretching it, the molecules should exhibit a tendency to return from their uncoiled and somewhat oriented state to a random, coiled arrangement. This process is, of course, not instantaneous. Rather, because of the high viscosity of the material, it is a process which should require considerable time. It is believed that the gradual decrease of load supported by doughs with increasing rest period between shaping and testing on the extensograph is a consequence of the process of randomization. The fairly rapid decrease of load with rest period is then due to the fact that molecules uncoiled and oriented by the shaping operation, are gradually returning to a random arrangement. Once this process is completed, the extensograph properties of the dough reflect the basic structure of the dough. However, if extensograms are drawn on a dough before this process of randomization is complete, there is superimposed on the basic extensograph dough properties, some residual effect of the molecular uncoiling and orientation.

It has been shown, in this work, that the fairly rapid decrease of extensogram load with increasing rest period can be characterized by an exponential decay law. This fact would seem to support the postulated process of randomization.

The Relaxation of Untreated Control Doughs

The relaxation curves obtained in each of the various experiments on untreated control doughs, when increasing reaction times between mixing and shaping were allowed, showed that the decrease of extensogram load with increased rest period was virtually constant. The relaxation curves for a given flour in a given experiment were almost superimposed. This is interpreted as an indication that no change in the basic structure of the dough occurred during these reaction times.

For the untreated control doughs for each reaction time, the rapid initial relaxation was succeeded by a slight, linear decrease of load with further rest period. This linear decrease of load with rest period is not likely due to a chemical change in the dough, such as proteolysis for example, since proteolysis should induce progressive change in the dough structure by degradation of the protein molecules, which would be expected to be reflected in a change in the rate of relaxation on the extensograph with increased reaction time. With the control doughs, however, the rate of relaxation with increased reaction time was observed to be constant.

The linear decrease of load with rest period may be due to a progressive softening of the dough with time, a behavior which has been observed by some workers. Halton (29, 30) noted that the force required to stretch a yeastless dough decreased as the age of the dough increased. This softening of the dough on standing was shown to be due to an increase of the free water content of the dough. Baker, Parker, and Mize (7), in studies of the supercentrifuging of doughs, concluded that the softening was a physical change accompanied by an increase in free water content and stated that all that was required to explain it was to assume a relaxation of the gluten from a strained condition caused by mixing.

The Relaxation of Bromated Doughs

The above interpretation of the molecular behavior of dough subjected to shearing action is useful in interpreting the changes in the physical extensograph properties produced by the action of potassium bromate. The incorporation of bromate into flour doughs was found to alter, more or less markedly, the rate of relaxation of doughs tested on the extensograph. For zero reaction time, the relaxation curves on bromated and unbromated doughs were quite similar in the region of the exponential decay of load, but when the reaction time was increased for doughs of a given bromate concentration, two distinct changes in the relaxation curves were noted. These were:

(1) the rate of relaxation decreased steadily with increasing reaction time,

(2) the final stable value of load supported by the bromated doughs increased progressively.

The linear decrease in the rate of relaxation of extensogram load with reaction time, as a result of the presence of bromate in the dough, can be explained in terms of the concept of randomization. The rate of relaxation may be interpreted as a measure of the rate at which the protein molecules, uncoiled and oriented by the shaping operation, tend to return to a random arrangement. The effect of bromate, then, would be attributed to changes in the dough structure which hinder the process of randomization.

It is postulated that the reaction of bromate in dough introduces certain linkages between the molecules of the network structure of the dough. The introduction of a bond between two elements of a polymer network will not only reduce the Brownian movement of the bonded elements but also the Brownian movements of nearly all the elements of the network (40). Hence, the introduction of such bonds into the network of the dough would result in a decrease in the rate at which the protein chains, uncoiled and oriented by the shaping operation, returned to a random arrangement.

The present study has shown that successive increments of bromate in dough produce progressively larger changes in the physical extensograph properties of doughs. When bread is baked with increasing increments of bromate, however, a different behavior is observed. It has been shown that with increasing increments of bromate in dough, loaf volume increases at first to a maximum, and then declines on further bromate addition (34). The fact that bromate damage occurs in bread is presumably a result of progressive changes produced in dough properties by bromate. The production of the maximum possible loaf presumably accompanies attainment of optimal dough properties at the time when the loaf is molded. If bromate is present in dough in amounts less than the optimum concentration, the dough properties are not at an optimum at the time when the loaf is molded, and as a result the maximum loaf is not attained. When bromate in excess of the optimum amount is present in dough, the gradual changes which occur in dough due to the reaction of bromate should occur at a higher rate, and the dough properties have progressed beyond the optimum required for bread-making before the dough is molded. When such a dough is molded, the pressure of the gas developed in the dough by fermentation after molding, though it be the same as in the previous two cases, may not be sufficient to cause the dough to expand into the maximum possible loaf. Experimental baking tests have actually shown that if a dough containing bromate in excess of the optimum is given a shorter fermentation period, i.e. a shorter reaction time for the bromate in the dough, a maximum loaf can be produced (53).

The experimental results showed that the reaction of bromate was not apparent, in terms of changes in extensograph dough properties, until the dough had been subjected to the shaping operation. The reaction of bromate in dough appeared to be latent, in the sense that only when the dough was shaped on the extensograph and the molecules uncoiled and oriented did the latent changes, which had taken place during the reaction time prior to shaping, become evident. This is in agreement with the observation by Baker and Mize that bromate has little effect in dough in the absence of mechanical action (6). It is suggested that the apparently latent effect of bromate corresponds actually to the production of potentially reactive centres in certain molecules, possibly protein, in the dough. Reaction of these groups does not take place in a resting dough at any appreciable rate, because the frequency of contact between the reactive groups of adjacent molecules is very small, owing to the lack of free migration of long chain protein molecules through the dough. However, when the dough is shaped on the extensograph, the dough molecules are uncoiled and aligned and tend to slide past one another as the dough is sheared in the shaping process. Hence, the shaping of dough serves to bring together the reactive groups formed during the time of reaction so that bond formation can result.

Certain of the data of the present study can be used quantitatively to confirm the above qualitative hypothesis of the reaction of bromate in flour doughs. Flour dough and gluten possess certain characteristics in common with elastomeric materials. The theory of the behavior of rubberlike materials has received much study in recent years and the structural concepts are well-developed. It is reasonable then, that some of the principles which have been formulated in the study of rubberlike elasticity might be adapted to study of the physical properties of dough and gluten.

The network theory of rubberlike elasticity predicts a linear relation between the force of retraction of a stretched polymer and the network structure, i.e. the degree of cross-linking. The relaxation curves for the bromate-treated doughs that had been allowed increasing reaction times show that the extensogram load decreased to a final stable value. The actual value depended upon the bromate concentration in the dough and on the reaction time. This final load in each case is believed to correspond to a steady state value characteristic of the network structure of the particular dough, and to be equivalent to the retractive force exhibited by a stretched polymer at a given elongation.

The experimental data of figure 10 for the change in rate of relaxation of extensogram load in bromated doughs with increasing reaction time, show that the reaction of bromate in doughs takes place at a steady rate. Further evidence for this may be found in figure 22 where the final stable load, as determined from relaxation experiments, is plotted against reaction time.

The stable load values are each regarded as a measure of a particular degree of cross-linking in the network structure of bromated

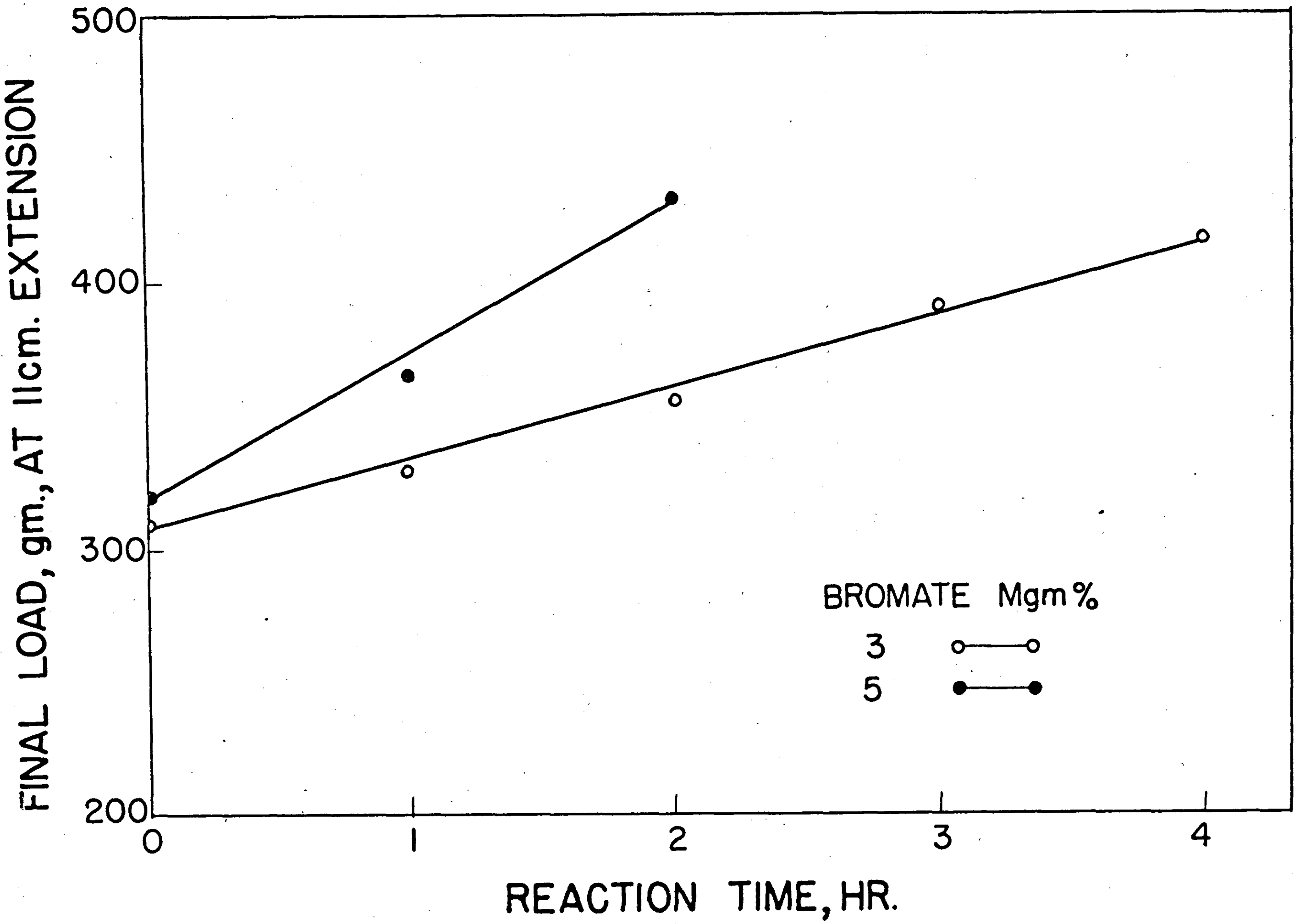


Fig. 22.

Curves showing the effect of reaction time on the final extensogram load supported by bromated doughs.

doughs and the curves of figure 22 as an indication of the rate at which the degree of cross-linking changed with reaction time in these bromated doughs. On this basis, cross-linking in dough occurs linearly with time, i.e. it is a zero order reaction analogous to that observed by Bardwell and Winkler in their study of the cross-linking of GR-S polymers with potassium persulfate (10). The curves of figure 22 do not pass through the origin because structures with a very low degree of cross-linking are not attainable in dough. The formation of a flour-water dough represents the minimum degree of cross-linking on which potassium bromate may exert its action.

Bardwell and Winkler showed that the rate of cross-linking in GR-S polymers was directly proportional to the concentration of the cross-linking agent, potassium persulfate. While the data for the reaction of bromate in dough are limited, they do tend to suggest that the rate of cross-linking in dough is directly proportional to the bromate concentration. These data are plotted in figure 23. The rate of cross-linking for bromate concentrations of 3 and 5 mgm. per cent are the slopes of the curves of the previous figure. This curve has been drawn through the origin since it was shown, in relaxation experiments on untreated control doughs, that the rate of relaxation did not change with increasing reaction time, i.e. that the degree of cross-linking of the network structure of the dough did not change with increasing reaction time.

It has been suggested that the decrease in rate of relaxation of extensogram load, due to the presence of bromate in dough, is the result of a progressive increase in the degree of the network

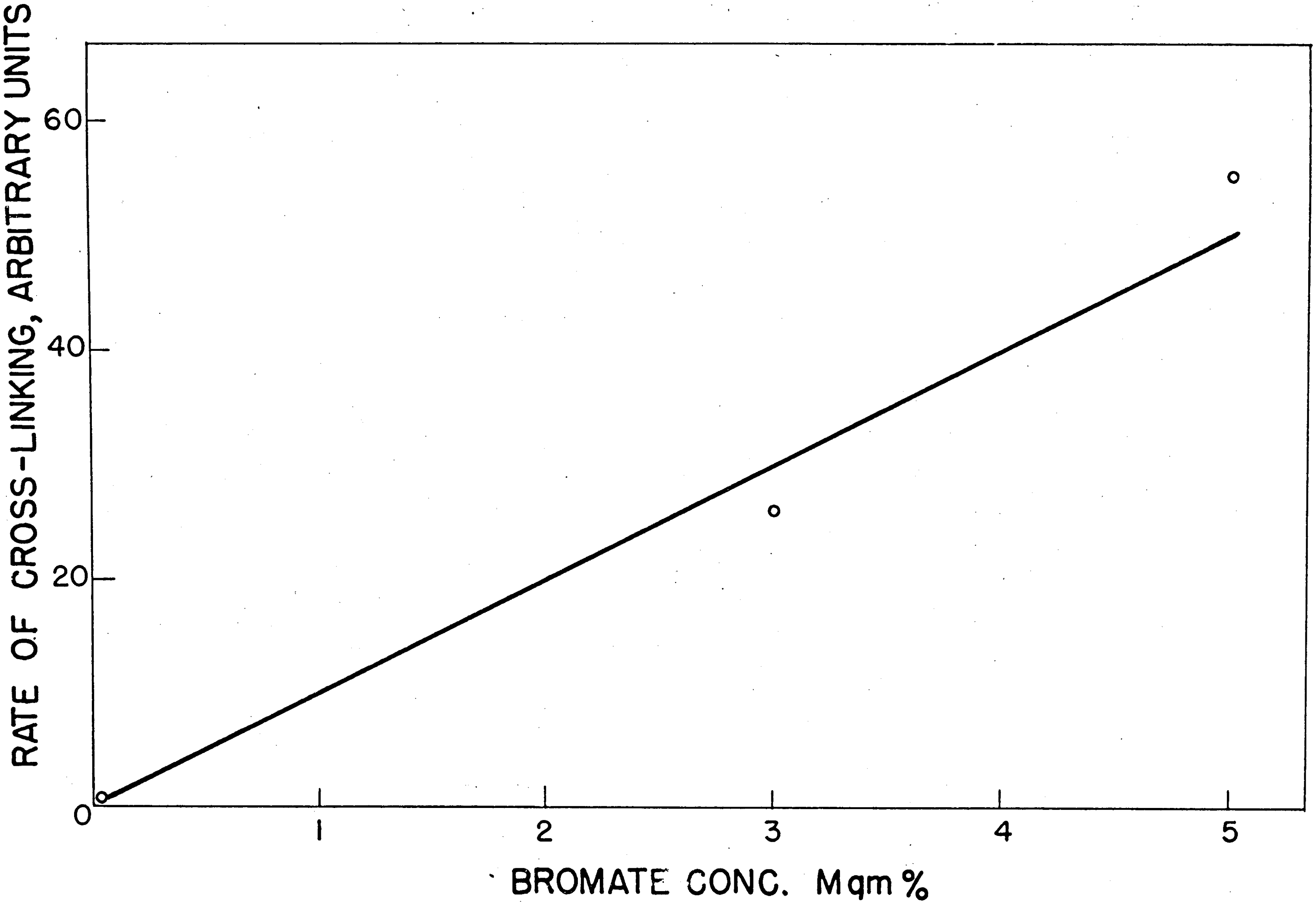


Fig. 23.

The effect of bromate concentration on the rate of cross-linking in dough.

structure of the dough. It has also been suggested, by analogy with the developments of rubber theory, that the increase with reaction time of the final stable load supported by bromated doughs is evidence of an increase in the degree of cross-linking in the network structure. If this is true, there should be some relation between the rate constant for relaxation, k, and the final extensogram load in the relaxation experiments. Figure 24 shows a plot of the rate constant for relaxation, k, against the final value of extensogram load for 3 and 5 mgm. per cent bromated doughs. These data are taken from Table VI.

The linear relation between the rate of relaxation of load, k, and the final load attained in relaxation experiments for the two bromate levels used would seem to confirm the qualitative postulate that the rate of relaxation is indeed determined by the extent of the network structure of the dough.

This type of approach to the study of the bromate reaction in dough should permit calculation of a value for the activation energy for the over-all changes that occur in the dough. In figure 25, the values of the final stable load, determined from relaxation experiments for 3 mgm. per cent bromated doughs, are plotted against reaction time for temperatures of 22.4°C, 30°C, and 35°C. These data are taken from Table XIV. The rate of cross-linking at a given temperature should be given by the slope of the final load - reaction time plot for that temperature. Although the data are inadequate for satisfactory calculation of an activation energy, they indicate a temperature coefficient for the over-all changes in the neighborhood of

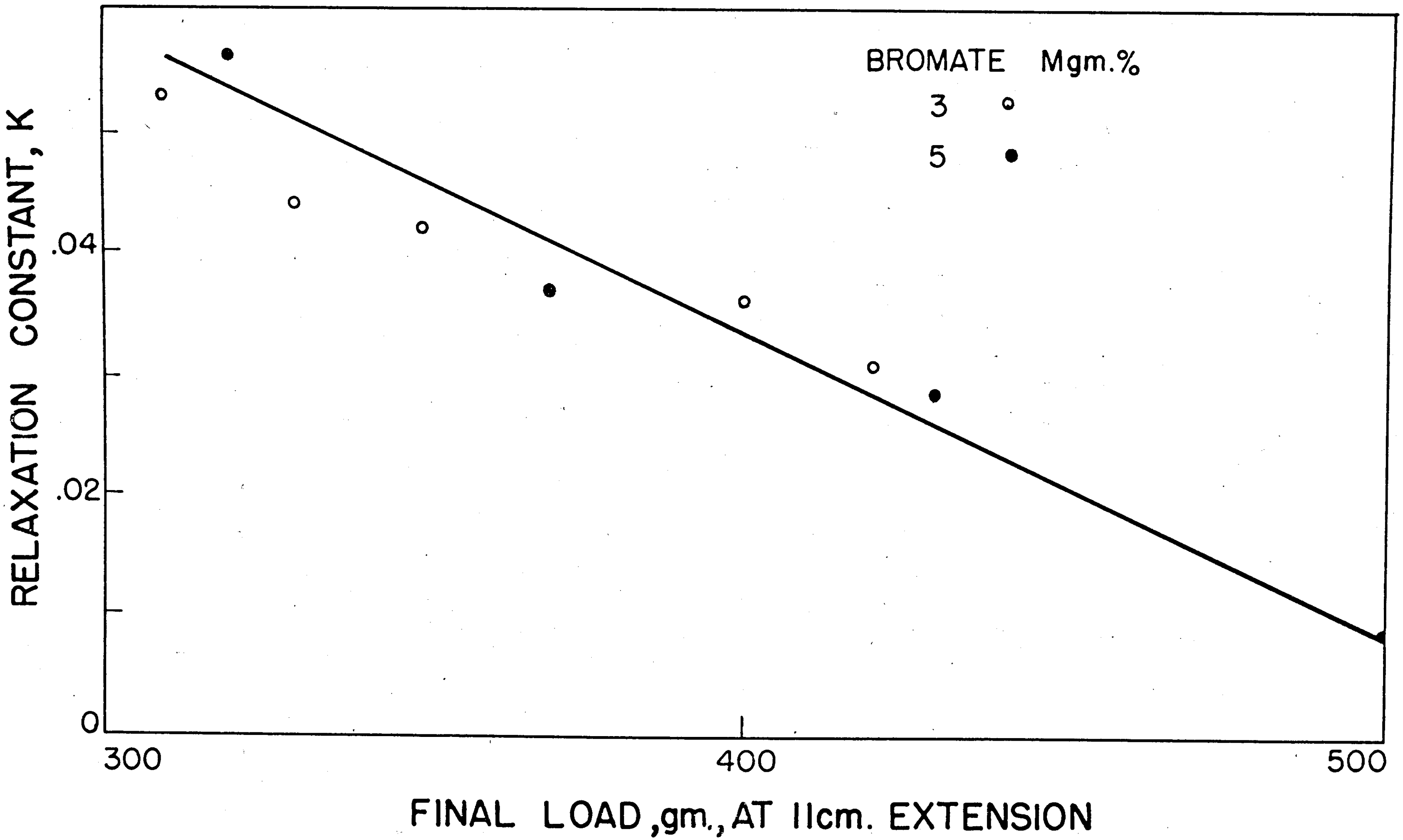


Fig. 24.

The relation between the rate of relaxation, k, and the final extensogram load supported by bromated doughs.

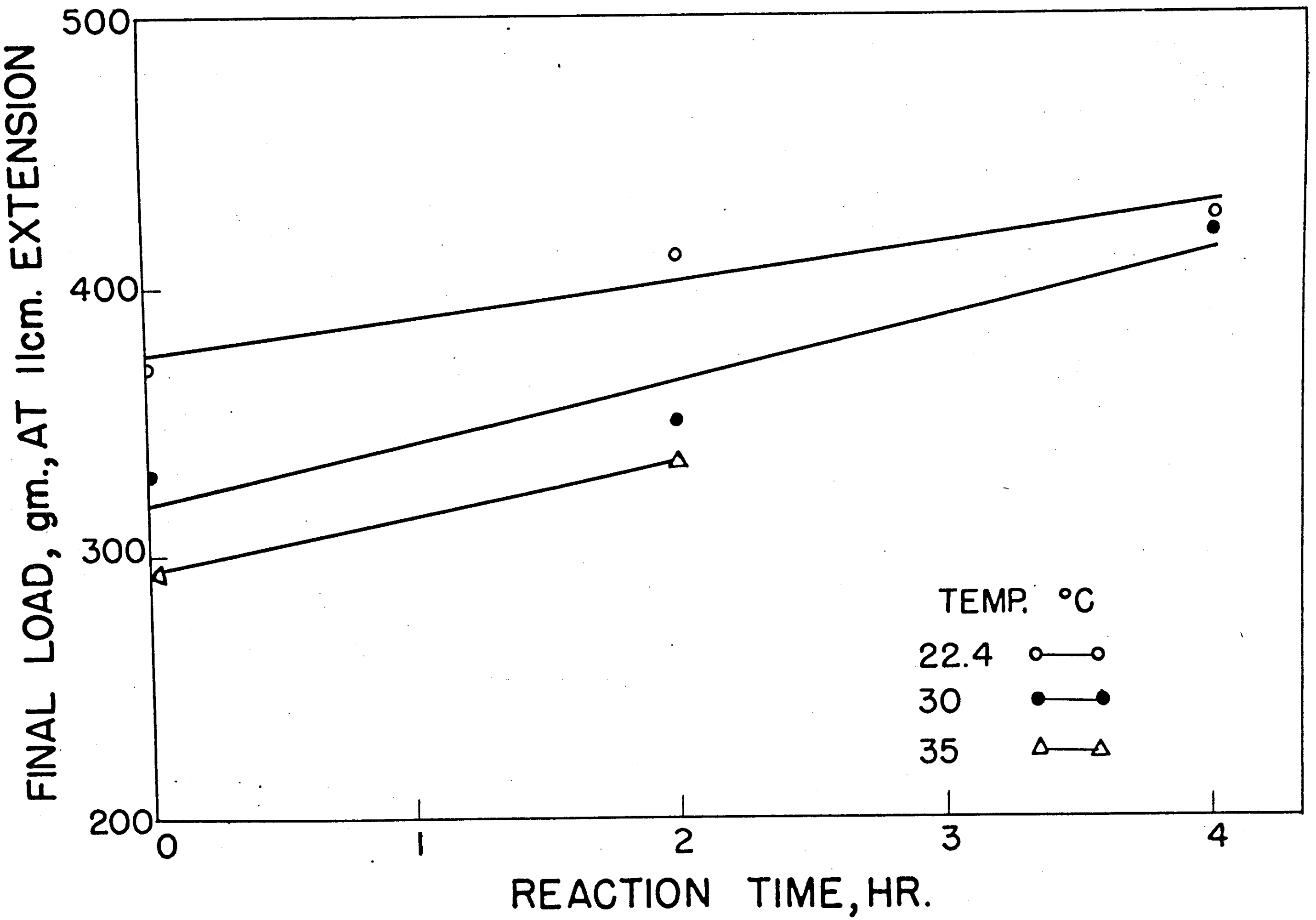


Fig. 25.

The effect of temperature on
the bromate reaction in dough.

11,000 cal.

While no emphasis should be placed on the value itself, the fact that the present approach to the problem permits such a calculation to be considered probably represents a significant achievement in the field of physical dough-testing.

The Effect of Oxygen on Physical Dough Properties

Experiments made by mixing doughs in oxygen showed that oxygen may produce effects in doughs which are similar in some respects to those resulting from the action of bromate. The data of Table XII showed that in relaxation experiments, the final extensogram load supported by oxygen-mixed doughs increased linearly with increasing reaction time. This is apparently contrary to the observation of Baker and Mize that the effect of oxygen on dough, in terms of the properties of the resulting bread, was confined to the mixing period, (5).

Actually, the two observations may not be as much at variance as appears at first sight. In the investigation by Baker and Mize of the effect of various mixing times in oxygen on bread properties using the experimental baking test, all doughs were given an identical treatment between cessation of mixing and molding the loaf of bread. This time interval, the fermentation period, was constant and actually constituted a reaction time during which any oxygen incorporated into the dough by the mixing action can react. The results of the relaxation experiments in the present study indicate that the reaction of oxygen takes place at a steady rate in dough. For such a reaction, the use of a single reaction time, with various initial oxygen concentrations determined by the mixing time, could lead to the conclusion that oxygen had an effect only during the mixing process. In fact, the studies of the effects on extensograph dough properties of varying the mixing time in nitrogen, air, and oxygen would, by themselves, lead to just such a conclusion. These data must not, however, be considered by themselves but together with the data of relaxation experiments to arrive at a correct interpretation of the facts.

The studies of the effects on extensograph dough properties of varying the mixing time of unbromated and bromated doughs in nitrogen, air, and oxygen yielded the further interesting result that bromate has an effect in dough which is independent of the mixing time.

The Effect of the Cupric Ion in Dough

Some information, which is useful in interpreting the effect of bromate in dough, was gained from the experiments in the presence of cupric ion. Copper was added in small amounts to the doughs because it was known to be an agent which can form linkages between certain groups in amines and amino acids (74). It was thought that if copper did indeed act as a cross-linking agent in the network structure of dough, the resultant changes in physical extensograph dough properties should be similar to those produced by bromate.

These experiments showed that copper does have an effect on dough properties which, in some respects, resembles the effect of bromate. For example, with increasing reaction time, copper produced a decrease in the rate of relaxation of extensogram load and an increase in the final stable load value, but the effect of copper reached a maximum in a reaction time of about 1 hour, after which no further effect was observed.

The fact that the effect of copper increased to a maximum with increasing reaction time suggests that copper reacts gradually with the dough, while the attainment of the maximum corresponds simply to completion of this reaction. The reaction of copper in dough, in terms of the resultant changes in physical dough properties, is not inconsistent with a process of cross-linking between certain dough constituents.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

Specifically:

1. The Brabender Extensograph, an empirically-designed physical dough-testing instrument, has been employed to study the reaction of potassium bromate in non-fermenting flour doughs as evidenced by changes occurring in physical dough properties.
2. The addition of successive, minute amounts of bromate to dough produces a progressively increasing change in the physical properties of dough as assessed by the routine extensograph test procedure.
3. The reaction of bromate in dough, as determined by relaxation experiments, takes place at a steady rate. Relaxation experiments are those in which the rate of decrease of extensogram load, with increasing rest period between shaping and testing doughs, is measured for doughs that have been allowed increasing reaction times between mixing and shaping. The greater the bromate concentration in dough, the greater is the change in the rate of relaxation with increasing reaction time.
4. Relaxation experiments showed that the capacity of bromated doughs to support a load decreased to a final stable value with increasing rest period between shaping and testing. The final load increased linearly with reaction time, and the higher the bromate concentration in the dough the more rapidly did the final load increase.
5. The reaction of bromate in dough is latent. Changes in the physical extensograph properties of dough due to the reaction of bromate were not evident until the dough had been worked after a reaction

period had been allowed. The reaction of bromate then showed up as a change in the rate of relaxation and also as an increase in the final value of the load supported by doughs in the relaxation experiment.

6. Oxygen, incorporated into dough by mixing, produced effects which in terms of extensograph dough properties were similar to those produced by bromate. The reaction of oxygen, like the reaction of bromate, was time-dependent and also appeared to take place at a steady rate. The final extensogram load supported by oxygen-mixed doughs in relaxation experiments increased linearly with reaction time.
7. The magnitude of the oxygen effect in dough was dependent upon the amount of mixing the dough received, corresponding to a dependence on the concentration of oxygen in the dough.
8. Mixing flour doughs in various atmospheres showed that bromate had an effect in dough in the absence of oxygen.
9. The addition of the cupric ion to dough produced changes in the extensograph dough properties which were somewhat similar to those produced by the action of bromate. However, unlike the changes produced in dough properties by bromate, those produced by copper increased to a maximum in about 1 hour reaction time, i.e. the reaction of copper in dough appeared to go to completion.
10. Since dough and gluten exhibit elastomeric properties, attempts were made to analyze the results of the empirical extensograph test in the light of developments in the field of high polymer chemistry.

11. Polymer concepts suggested that the final stable extensogram load supported by doughs in relaxation tests was equivalent to the force of retraction in stretched polymers, which is a function of the network structure. The final stable extensogram load was then assumed to be a measure of the degree of cross-linking in the network structure of the dough. The change in the final extensogram load with increasing reaction time was taken as a measure of the rate of cross-linking produced in the network structure of dough by added agents.
12. The application of polymer concepts to the study of changes produced in the physical properties of dough permitted quantitative use of data derived from the empirical extensograph test. This approach confirmed the conclusion which had been deduced from the changes in rate of relaxation of bromated doughs with reaction time that the bromate reaction took place at a steady rate in dough.
13. The rate of cross-linking in the network structure of dough appeared to be linearly related to the bromate concentration in the dough.
14. The activation energy for the reaction of bromate in dough was in the neighborhood of 11,000 calories.

Generally:

The present investigation is by no means the first in which the extensograph has been used in studying the changes in physical properties of doughs produced by small amounts of added reagents. Even the essentials of the technique, i.e. the use of the extensograph to follow the decrease of the load supported by doughs with increasing rest period between the shaping of a dough and subsequent testing, have been used at least once (56). This was in a preliminary investigation of the suitability of the instrument for the routine testing of flour doughs. However, so far as the author is aware, the present study constitutes the first systematic attempt to derive data from the results obtained with this empirically-designed instrument, which could be employed in a quantitative manner to yield information about the reactions responsible for the observed changes in behavior. This study involved, on the one hand, consideration of certain important physical properties of dough and gluten, such as the rubber-like elasticity of dough and the limited swelling of gluten. On the other hand were involved certain of the fairly well-developed structural concepts of high polymer chemistry. The application of some of the principles of high polymer chemistry to the study of the changes in the physical properties of doughs, as revealed in tests with the extensograph, enables special significance to be attached to certain aspects of the empirical results.

This study is by no means complete. Rather, it represents a promising approach to the possibility of placing the whole field of physical dough-testing on a sound scientific basis, and in this way, presumably represents a significant advance in the field of Cereal Chemistry.

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