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FLOUR BLEACHING

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FLOUR BLEACHING.

HARRY SNYDER.

Bleaching a Natural Process. It is well known among millers and bakers that flours when stored undergo changes resulting in slight bleaching and improvement in bread making value. In a former bulletin of this station (No. 85) the results of experiments are given showing the influence on bread making value of storage. It was found that: "A slight bleaching had resulted from storage. The freshly milled samples were not as light in color as the stored samples." There was also an improvement in bread making value. "The flours that had been stored four and eight months respectively produced a somewhat larger loaf than the freshly milled samples." There was no appreciable difference in composition between the freshly milled and the stored samples other than in moisture content. In the case of the spring wheat flour the loss from drying was equivalent to about two pounds per hundredweight of flour. In conclusion it was stated: "In these tests a slight improvement resulted from storage of the sound flours." The improvement is ascribed to the action of enzymes which are known to be present in wheat. In order to secure the full advantage resulting from the curing of flour by storage, the flour must be well milled, the wheat thoroughly cleaned and all debris particles of a fermentable nature removed, otherwise flour when stored becomes unsound through fermentation changes.

In the literature on flour and bread making there are frequent references to the bleaching of flour by natural agencies as light and air and the changes incident to storage. Jago states that bleaching takes place in the absence of light. Avery reports that the yellow coloring matter of flour dissolved with the oil is bleached by exposure to light and that when flour is placed in a thin layer between plates of glass and exposed to both direct and reflected sunlight, bleaching results.

The bleaching of flour then is a natural process and is associated with aging and curing. It would not be possible to secure the benefits of aging and curing without bleaching also taking place. Many flours do not possess their maximum bread making value until after the aging and curing process. Why there should be a difference in bread making value of cured over freshly milled flour has never been determined. Similar facts have been observed in connection with flour made from new and old wheats, the old and cured wheat yields a flour of higher bread making value than the new.

The Coloring Material of Flour. The chemical changes which take place when flours are cured by storage in a warehouse have not been determined. One of the changes is in color. The composition of the coloring matter of wheat has never been determined because it can not be separated in a pure state from the fat and gluten with which it is mechanically associated. It is soluble in ether and in flour analyses it forms one of the well known impurities of the "ether extract" or "crude fat." When the gluten is obtained mechanically, by washing the dough, it is tinged yellow with the natural coloring matter of the flour.

Avery has suggested that the coloring matter of flour is a nitrogenous compound containing an amino radical. In bulletin No. 85 of this station it was suggested that the coloring matter was a nitrogenous compound. Other investigators believe it is a non-nitrogenous body akin to xanthophyll and carotin, the natural yellow pigments of plants. It has certain characteristics of carotin as capability of being decolorized by heat, light and chemical reagents. Whatever the composition of the coloring matter of wheat may prove to be, it is not a stable compound. In dealing with flour, color is a variable property and it can be considered a permanent characteristic only after the coloring matter has undergone a permanent change as secured by the aging and curing process resulting in bleaching, and when the flour has reached its maximum bread-making value. In all intermediate stages, color is variable. The color of flours is generally taken as an index of quality as it indicates the character of the wheat from which the flour was produced and the extent to which the aging and curing process has been carried. The color is not a characteristic which is capable of being determined as accurately as could be desired. Color tests are not generally regarded by chemists as among the most accurate tests for determining the character of materials. In discussing the color of compounds from a chemical point of view, Mulliken in "Identification of Pure Organic Compounds" says (page 230):

> "Careful analysts have always very properly refused to attach the same importance to verbal descriptions of subjective color phenomena as a means for specific characterization, that they willingly grant to the recorded values of melting-points, boiling-points, specific gravities, and other physical constants whose determination requires the use of comparatively slow and elaborate methods of measurement.
>
> "The chief causes for the disrepute into which color tests have fallen are: the customary failure, except in spectroscopic work, to refer colors to any well-defined standard; the loose use made of the terms constituting the popular nomenclature of color; the imperfect development of the color memory; and, finally, the frequent omission of minor but essential experimental details from the directions given for the performance of color reactions."

While in a general way the changes in color which take place when flour is cured may be described, it is not possible to measure them with the same degree of accuracy as in the determination of other characteristics. After flour has undergone natural bleaching various tints and shades of color are developed, particularly of grey and light yellow. These various shades and tints may serve as an index of bread making value, but it is not possible from the color alone of either freshly milled or cured flour to determine bread-making value. Flours that are pure white, or tinged slightly yellow have the highest bread-making value. A dark grey or slaty color is usually an index of poor bread making qualities. Flours of poor color when milled, often develop even more undesirable tints by storage. If the flours are not well milled the brany particles become discolored through oxidation of the cellulose and the flours then show black specks. Hence it is that only well milled flours from sound wheat are capable of being improved by storage.

Bleaching Reagents. Since flour is bleached and otherwise improved in its bread-making value by storage, various attempts have been made by the use of bleaching reagents to imitate and hasten the process so as to dispense with storage. The use of chlorine gas was one of the first reagents proposed for the purpose and a patent was issued in Great Britain about thirty years ago. Later the use of sulphur and ozone were proposed. Pure oxygen except in its active state, as when liberated from chemical combination, has been found to have no appreciable bleaching action, but when it contains minute traces of chlorine and other elements, bleaching readily takes place. None of the earlier methods for bleaching were commercially successful because they injured the bread-making value of the flour.

As an illustration of the action of such bleaching reagents, experiments made at this station and reported in bulletin No. 85 are cited. In these experiments oxygen gas made from heating potassium chlorate was used as the bleaching reagent. The bleaching was undoubtedly due to the traces of chlorine or oxides of chlorine which the gas contained and not to the oxygen. With this bleaching reagent, a slight loss in bread-making value resulted. As reported the loaves produced from the bleached flour "although whiter in color were smaller in size, and less in weight." The gluten appeared to have been slightly oxidized and possessed less power of expansion and absorption. These bleaching experiments were made and reported prior to the discovery and introduction of the present electrical methods of bleaching now generally practiced in the manufacture of flour in this country. It was noted that "in the bleached flours, dust particles and debris are more readily discernable as they blacken by oxidation instead of bleaching," indicating that the bleaching of low grade and poorly milled flours was not practicable, as bleaching only tended to make the impurities more prominent. The bleaching with chlorine was carried to the extent of destroying the natural color of the flour and resulted in a color which would not have been produced had the flours been allowed to undergo the process of aging and curing by storage. The object of all of the earlier methods of flour bleaching was apparently to whiten the flour without securing any of the other beneficial effects incident to aging and curing.

Modern flour bleaching is of comparatively recent origin. The extensive use of nitrogen peroxide as a bleaching reagent dates mainly from 1904, when air containing traces of nitrogen peroxide gas produced by a flaming discharge of electricity was found to effectually bleach flour. For a few years prior to this nitrogen peroxide generated by chemical action had been used to some extent in European countries. Of the various methods proposed for the bleaching of flour practically the only one that has survived the experimental stage is the nitrogen peroxide process in which the bleaching reagent is produced directly from the union of the nitrogen and oxygen of the air by electrical action.

Electrical Method of Flour Bleaching. When a current of electricity is passed through air, chemical combination takes place between a part of the nitrogen and oxygen which are the main constituents of the air. This fact has long been known, and it is now being utilized to some extent for securing combined nitrogen as a fertilizer for crops as wheat and other cereals incapable of making use of the free nitrogen of the air. The active material which causes bleaching of the flour is nitrogen peroxide, formed either directly by the union of the nitrogen and oxygen or as a secondary product resulting from the action of air upon nitric oxide. The amount of nitrogen peroxide gas required for flour bleaching is exceedingly small. Alway reports that 5 c. c. and less of the gas mixed with three liters of air will effectually bleach a kilogram of flour. On a percentage basis this would make the bleaching mixture consist of over 99.9 per cent air. Nitrogen peroxide gas forms with water both nitrous and nitric acid. Theoretically two parts of the gas unite with one of water to form one part each of nitrous and nitric acids. Analysis of the air from an electrical machine as it is delivering gas for bleaching purposes shows the presence of both nitric and nitrous acid products as nitrates and nitrites.

In order to study the composition of the bleaching gas and its effects upon flour, a small electrical flour bleach-

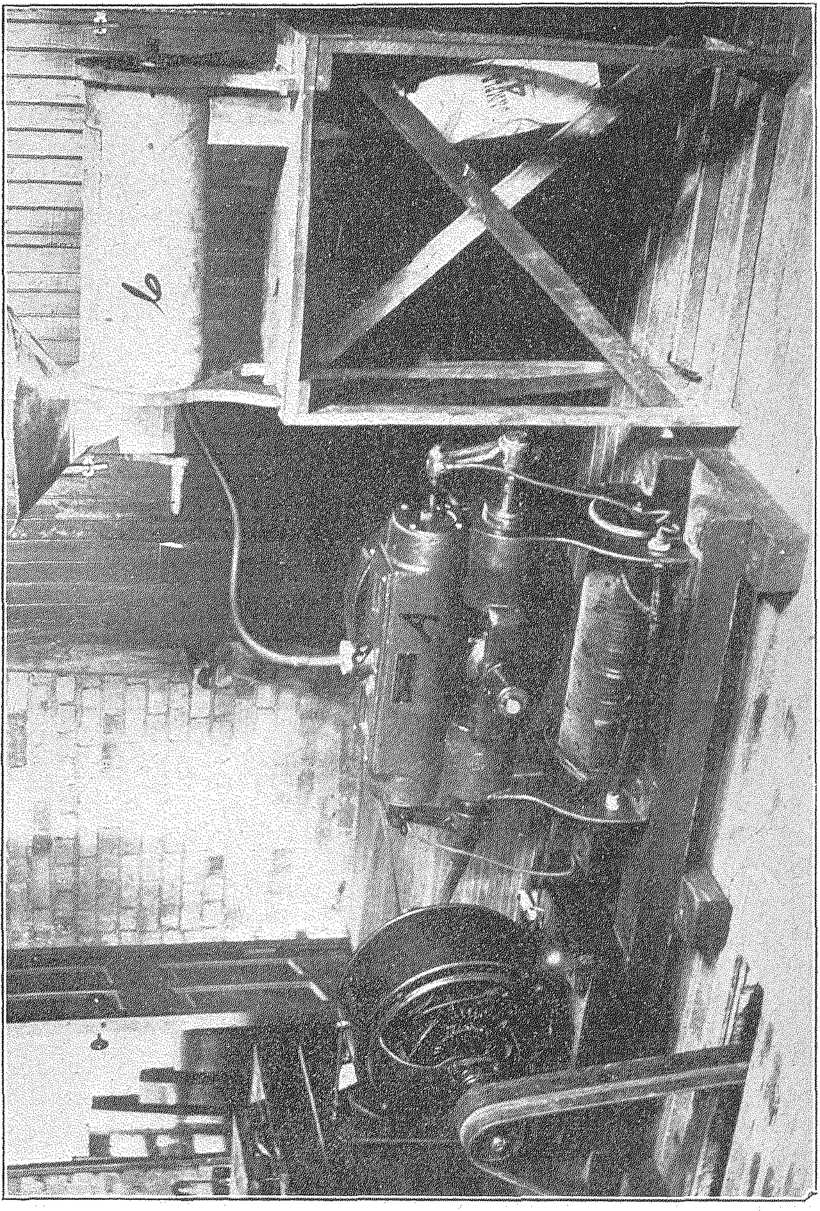

Fig. 1.—Electrical apparatus used in flour bleaching.

ing machine was rented and operated in connection with the experimental flour mill of the Minnesota Experiment Station. An analysis of the gas as delivered for flour bleaching purposes was made. An illustration of this device used for the electrical bleaching of flour is given in Fig. No. 1. A current of electrictiy is passed through the air in cylinder A. The current is alternately broken so as to make a flaming discharge. This is accomplished by means of the copper rods 1 and 2, operated by a suitable mechanical device. As result of the flaming discharge of electricity, which is practically a miniature flash of lightning, a chemical compination of a small portion of the nitrogen and oxygen of the air takes place. The trace of peroxide of nitrogen formed is immediately forced out of the cylinder through outlet B, and a fresh quantity of air is drawn into the cylinder. The air which has been electrically acted upon and as a result contains a minute amount of nitrogen peroxide, is then forced into the cylinder C where it is brought in contact with the flour which is being agitated the while. Bleaching is immediately effected, the flour and air containing the bleaching reagent being left in contact from 10 to 30 seconds. The air and gas as delivered through C have a slight odor similar to that perceptible around electrical machines used in class room experiments in physics and a temperature of 48° to 50° C.

Attempts were made to determine from the total nitrite and nitrate reacting substances the amount of nitrogen peroxide formed. The nitrites were determined with a high degree of accuracy by the Greiss-Ilsovy method, by means of which may be detected one part of nitrite reacting substance in one thousand million parts of the material. Unfortunately the mehods for determining nitrates do not admit of such a high degree of accuracy, and hence when the nitrogen peroxide breaks up into nitrite and nitrate reacting substances, one of the products—the nitrite—can be more accurately determined than the other. Duplicate determinations when the electrical machine was running at full capacity gave the following results:

1. 1 litre air contained .000219 grams nitrogen as nitrite.
2. 1 litre air contained .000192 grams nitrogen as nitrite.

Average, .000205.

Properties of Nitrogen Peroxide. Pure nitrogen peroxide is a reddish brown gas. At a temperature of 75° F. it is a mixture of two compounds, N_2O_4 and NO_2. Remsen gives among the properties of nitrogen peroxide the following: "It acts energetically upon compounds which have the power to take up oxygen." When this takes place the nitrogen peroxide is reduced to nitric oxide, a colorless gas. One of the most characteristic properties of nitric oxide is its ease of combination with oxygen to form nitrogen peroxide. Nitrogen peroxide is one of the most efficient carriers of oxygen known. It readily gives up a part of its oxygen to substances which are unable to take this element directly from the air, and in turn immediately unites with a fresh portion of atmospheric oxygen. In this way a small amount of the gas is capable of effectually acting as a bleaching reagent, while the gas itself does not enter into chemical composition with the flour. This property of nitrogen peroxide, as a "carrier of atmospheric oxygen," is well known and is described in nearly all text books on general chemistry. It is made use of in the arts and in manufacturing operations. Newth (Inorganic Chemistry) describes this action of nitrogen peroxide as follows: "Sulphur dioxide is unable to absorb an additional atom of oxygen, and so pass into sulphur trioxide without the aid of some third substance, which can act as a catalytic agent, or a carrier of oxygen. The material which is employed for this purpose is one of the oxides of nitrogen, which is capable of giving up oxygen—and of again taking up oxygen from the air. Thus, nitrogen peroxide (NO_2) by the loss of one atom of oxygen, is reduced to nitric oxide, NO; which in its turn combines with atmospheric oxygen, and is reconverted into nitrogen peroxide." "The nitrogen peroxide at the end of the reaction is unchanged, and is able to react in the same series of changes over and over again."

In the bleaching of flour the unstable yellow coloring matter is acted upon by the nitrogen peroxide, and from a study of the properties of nitrogen peroxide it would appear to be an oxidation change. As will be shown later, this change if it be oxidation, does not extend to the other constituents of the flour as fat and gluten, inasmuch as flour bleaching as now practiced leaves these and other constituents unaltered as far as chemical tests are capable of determining. Other than a possible oxidation of the coloring matter the trace of nitrogen peroxide used in the bleaching mixture appears to induce simply catalytic changes. The gas itself, or any of its derivatives or component parts, does not enter into chemical combination with the flour after perfoming its role as a carrier of oxygen, as practically all of the gas used as the bleaching reagent can be accounted for either physically combined with the flour or present in the air of the bleaching medium after the operation.

Absorption of Nitrite Reacting Materials by Flour. Many solids possess the property of physically absorbing gas with which they come in contact. Jones (Elements of Physical Chemistry) in discussing solutions in solids, says:

> "*Solutions of Gases in Solids.*—Many solids have the property of dissolving gases in large quantities. Thus, charcoal dissolves large volumes of carbon dioxide, palladium hydride dissolves hydrogen, etc. Our knowledge of such solutions is almost limited to the fact that they exist. It is known, however, that the greater the pressure to which the gas is subjected, the larger the quantity which will be absorbed by the solid. In speaking of solutions of gases in solids we mean, as in all other cases of true solution, those in which there is no chemical action between the gas and the solvent. The fact that gases can form solutions in solids is often utilized to remove the gas from regions where it is not desired. The solubility of a gas in a solid may be very great, indeed, as in the case above mentioned of carbon dioxide in charcoal."

Independent of any chemical combination, it would naturally be expected that traces of the bleaching gas would be present in the flour. That nitrites are present is readily shown by testing the aqueous extract of flour for nitrites by the delicate Greiss-Ilsovey method. In just what form this nitrite reacting material is present in flour is not known. For convenience it is called a nitrite, but as will be shown later it is not present as a mineral nitrite like sodium or potassium salts, as it has entirely different properties from either. It can scarcely be regarded as free nitrous acid, as this acid is so unstable that it is incapable of existing in nature in a free state for any length of time. Most authorities state that nitrous acid in a pure state has never been separated and it exists only theoretically in aqueous solution.

Amount of Nitrite Reacting Materials in Flours. Flours purchased on the market, bleached by electrical processes generally yield upon analysis from .3 to .8 parts of nitrogen, as nitrite reacting material, per million parts of flour, the average is about .4 parts per million. In three cases, one part per million has been found. As previously stated this nitrite reacting material is in physical and not in chemical combination with the flour. Expressed on a percentage basis it is equal to .00004, that is in 100 grams of flour there are .00004 grams of nitrite nitrogen, or .4 of a milligram per kilogram of flour.

The most delicate analytical balance is sensitive to .1 of a milligram when carrying its maximum load of 200 grams. The average amount of nitrite nitrogen present in 200 grams of commercially bleached flour, the maximum quantity that can be weighed at one time, is less than can be indicated upon an average analytical balance. It is present in an unweighable quantity and it can therefore be consistently designated as an infinitesimal amount. That the material is present largely in physical form can be shown by heating bleached flour to a temperature of 95°C. The flour will then be found free from nitrite reacting material provided it has been heated out of contact with a gas flame or combustion products that yield nitrites, or the flour was made from wheat free from mineral nitrates or nitrites. Alway has shown that when a large excess of gas is used experimentally for bleaching purposes, the quantity of nitrites retained in the flour after the lapse of a few weeks is no greater than when medium amounts are used. There appears to be a limit to which it is possible for flour to physically absorb and retain nitrogen peroxide products. The influence of different quantities of gas in the bleaching of flour is discussed in another part of this bulletin.

Fat of Bleached and Unbleached Flour. In order to determine if the traces of nitrogen peroxide used in the electrical bleaching of flour had any chemical action upon the fat, the iodine number, nitrogen content, heat of combustion and other characteristics of the fat from flours before and after bleaching were determined. When the fat of flour is obtained by the official method of analysis, the coloring matter, lecithin, chlorophyll residue products and other substances are recovered as mechanical impurities mixed with the fat. The chemist uses the term "crude fat" or "ether extract" because of these known impurities. Some of the impurities are nitrogenous and some are non-nitrogenous compounds.

> "In their pure state the fats and oils are odorless, colorless and tasteless; and what is usually regarded as characteristic in these respects of the different oils and fats is really due to the presence of small quantities of foreign substances. On exposure to sunlight (and to air) even strongly colored oils are gradually bleached, some oils becoming almost colorless."—(Lewkowitsch, "Chemical Analysis of Oils, Fats and Waxes," page 9.)

In discussing the composition of fats and any possible changes which may occur through the action of traces of nitrogen peroxide, the impurities associated with the fats must be considered also. If it were possible to obtain the fat in an absolutely pure state the problem would be much simplified, as then any change which was found to have occurred could be definitely ascribed to the fat. As previously stated the natural coloring matter of flour is acted upon by natural agencies as air and light and is also readily bleached by traces of nitrogen peroxide. Hence change in the color of the fat produced by bleaching can not be said to denote change in the composition, when it is known that the color is one of the impurities of the fat. Fats are compounds characterized by containing a relatively large amount of carbon and a small amount of oxygen. When exposed to the air fats undergo an aging or curing process which has been extensively investigated by Sherman, who has found that both animal and vegetable oils are "altered by age or oxidation." Oils kept for a long time in contact with air "take up atmospheric oxygen, and gradually become considerably altered in these constituent properties which are commonly regarded as constants." "It is evident that the oils that are altered are very likely to be misjudged, especially if only one or two quantitative determinations are made."

In the bleaching of flour it has been suggested that a slight oxidation of the fat is one of the possible chemical changes which may occur, since nitrogen peroxide, a carrier of atmospheric oxygen, is employed. Should any appreciable oxidation of the fat take place during bleaching, the fat of the bleached flour would have different properties from that of the unbleached flour. Any chemical change affecting the fat would necessarily show itself in some of the determinations, as iodine absorption number and heat of combustion. Wheat fat will combine with about an equal weight of iodine and has an iodine absorption number of about 100. When the fat is exposed to air in a thin layer and dried, it readily undergoes oxidation. This renders the determination of the iodine number difficult as it is necessary in order to accurately weigh the fat that it be free from water. When the fats are oxidized by natural drying they show a much lower iodine absorption number. Four typical samples of flour (two bleached and two unbleached) were finally selected for the purpose of extracting the fat in quantity. The flours were dried in such a way as to prevent oxidation, and the iodine number was determined. The following results were obtained:

	Iodine Absorption Number.
Patent flour, unbleached, No. 1	102.9
Same flour, bleached, No. 2	103.7
Patent flour, unbleached	101.1
Same flour, bleached	102.6

Practically no greater differences were observed between the fat of the bleached and unbleached flours than between duplicate analyses of the same sample. As far as the iodine number of the fat is concerned no appreciable difference was observed between those of the bleached and unbleached flours.

In order to still further check these results samples of these bleached and unbleached flours were sent to Prof. Sherman, of Columbia University, to determine the iodine number and index of refraction. He reported the same iodine number for the fat extracted from each of the flours namely

103. Where samples of the oil extracted from these flours had suffered slight exposure in course of extraction, they gave iodine numbers from 91 to 101. Prof. Sherman reported: "I do not consider that my results establish any significant difference between the oils of the samples of flour, Nos. 1 and 2." In earlier investigations the iodine number of the fat from flour and from bread was determined. The results are published in bulletin No. 67, Office of Experiment Stations, U. S. Dep't. of Agr.: "The iodine absorption number of the fat of flour and from the bread was determined. That of the fat from the flour was 101.4 and that of the fat from the bread, 60.4."

Briefly stated, the traces of nitrogen peroxide used in the electrical bleaching of flour affects the coloring matter, an impurity of the fat, but does not affect the fat itself. Should slight oxidation occur, incapable of detection by analysis, it would probably be no greater than would naturally take place when flour is exposed to the air and the fat undergoes "natural aging and curing." In the process of bread making the fat is oxidized and should slight oxidation occur during electrical bleaching or storage it would in no wise affect the nutritive value, as this same change occurs and to a considerable extent when flour is made into bread.

It has been suggested that the nitrogen peroxide chemically unites with the fat resulting in the production of nitrogenous compounds. Should any such change occur it would affect the nitrogen content of the product, and the fat from the bleached flour should show a higher nitrogen content. A number of investigators have shown that lecithin, a nitrogenous compound soluble in ether, is present as an impurity in the ether extract or crude fat obtained in the analysis of flour. Hence it is, wheat fat as ordinarily obtained contains nitrogenous compounds rendering it exceedingly difficult if not impossible to separate from that naturally present any new nitrogenous compound that may possibly be formed during the process of bleaching. The ether extract or crude fat of three samples of unbleached flour was obtained in quantity by extraction with one of the best grades of commercial ether. Also the ether was purified as directed in the official method of analysis and the nitrogen content of the crude fat extracted with the purified ether by the official method was determined.

NITROGEN CONTENT OF FAT OF UNBLEACHED FLOURS.

Sample	Commercial Ether.	Purified Ether.
1	.887	.873
2	.919	.901
3	.931	.942

It is to be noted that approximately .9 of a per cent of nitrogen was found present as a natural constituent of wheat fat. There was no difference in the results whether the ordinary or the modified Kjeldahl method was used for determining the nitrogen content of the fat. In determinations (qualitative or quantitative) of the nitrogen content of the fat of bleached flour, the nitrogen that is naturally present must be recognized, and the presence of nitrogenous compounds in the fat can not be ascribed to bleaching. The nitrogen content of the fat of three samples of flour before and after bleaching was determined with the following results:

	Nitrogen of Fat.	
	Bleached.	Unbleached.
Flour A	.866	.887
Flour B	.930	.919
Flour C	.927	.931

Duplicate determinations were made and no greater differences in the nitrogen content of the fats from bleached and unbleached flours were found than between duplicate analyses of the same sample. The quantitative determinations of nitrogen showed the bleaching of the flour did not increase the nitrogen content of the fat. As in the case of the iodine number so with the nitrogen content any change occuring during bleaching is insignificant and is less than is capable of being determined by chemical analysis.

The heat of combustion of the fats was also determined in a Berthelot calorimeter and practically the same caloric value was obtained for the fat from the bleached as from the unbleached flour. The differences in the heats of combustion were no greater than in the case of duplicate determinations on the same sample. If any oxidation or nitration had taken place during the process of electrical bleaching, it would have manifested itself in lowering the heat of combustion. Neither the iodine number, nitrogen content nor heat of combustion shows any change to have occurred; or that the fats from bleached and unbleached flours differ.

The Glutens of Bleached and Unbleached Flours. The gluten from average commercial bleached flour is lighter in color than that from similar unbleached flour, in all other respects, however, the glutens are alike. Numerous determinations were made of the nitrogen content of bleached and unbleached flours and in no instance was any increase observed when the results were calculated on a dry matter basis. Occasionally there is apparent increase in nitrogen due to loss of water, and the bleached flour then contains a larger amount of dry matter which is proportionally richer in gluten because of the loss of water. One of the claims originally made for the bleaching of flour was that some of the starch was changed to gluten by the electrical action, but the work of a number of investigators has shown the fallacy of this claim, and that bleaching does not increase the total nitrogen content of the flour.

Wheat gluten is composed of two proteids, gliadin and glutenin, the former is soluble in 70 per cent alcohol and has definite physical characteristics. When a solution of gliadin from a bleached flour was examined with a polariscope, the same reading was secured as when some of the same flour, unbleached, was examined. Had any chemical change occurred during bleaching affecting the composition of the gliadin it would have resulted in changing the polariscope reading. The specific rotation of gliadin from bleached and unbleached flour was found to be identical.

It would not be possible for nitro- or nitrosyl-compounds to be formed during bleaching because not enough nitrite or nitrate reacting materials are present to permit such reactions taking place. Furthermore nitrous and nitric acids if present in sufficient amounts to cause a reaction would produce yellow colored products in accord with the well known xantho-protein reaction of Fourcroy and Vauquelin. The nitro-derivatives of the proteins, particularly the glutens are all yellow colored. If such compounds were formed, bleaching could not take place. It takes about two hundred times more nitric oxide gas to produce a light yellow color in flour, resulting in the formation of nitro-substitution products of the proteids, than is required for bleaching. There is no danger of treating flour by the electrical generation of nitrogen peroxide to such an extent as to result in the formation of nitro-substitution products as the gas is too dilute to permit of such a reaction, and furthermore, should the change occur the flour would be injured for commercial processes as it would have a yellow color. Such a procedure would be directly opposite to bleaching, and in that event the nitrogen peroxide would act as a stain and not as a decolorizing reagent. Nitrous and nitric acid products are extensively used in the arts for the preparation of yellow dyes, as for the coloring of woolen and silk cloth, but when thus used enough is required to chemically unite with the albuminous material of the cloth to form a new compound in accord with the law of definite proportion. This result can not be secured from the use of an infinitesimal amount. The trace of nitrogen peroxide employed in the bleaching of flour can not be regarded in any way as a dye or stain, as it does not unite chemically with either the fat or the gluten, or form a coating over the surface of the flour particles. Its action upon the coloring matter of flour is similar to the change that takes place naturally when flour is cured and bleached by storage.

Physical Absorption of Gas by Flour. Since analyses of the fat and gluten of bleached flour indicated that no chemical combination had taken place with the trace of nitrogen peroxide used in the bleaching mixture, experiments were undertaken to determine whether the nitrite reacting material in the bleaching gas could all be accountd for as absorbed in the flour. Three series of tests were made. Nitric oxide was produced by chemical action, and the purity of the gas determined by analysis. In the first series a given volume of the gas was added to a glass flask containing 200 grams of fine purified quartz sand. The sand, air and gas mixture was well shaken for 1½ minutes. Then the air in the flask was aspirated through absorption bottles to collect any nitrites that had escaped absorption by the sand. The sand contained some water. The soluble nitrite material in the sand was then determined, the following results being secured:

	Grams.	Grams.
Nitrogen as nitrite reacting material in gas used	.001205	
Nitrogen as nitrite reacting material in sand		.00106
Nitrogen as nitrite reacting material in air not absorbed		.00010
Total		.00116
Mechanical loss and error		.000045

The larger portion of the nitrite reacting material in the gas was physically present in the sand and was absorbed by it. The pure silica, SiO_2, is incapable of chemically uniting with nitrogen peroxide and the absence of any bases as sodium or potassium prevented the formation of any of the mineral nitrites. The nitrite reacting material in the sand is simply in physical combination. Other tests showed similar results, the amount absorbed by the sand depending upon the amount of moisture present. In the case of dry sand a small amount was absorbed.

In the second series of experiments flour was substituted for sand, and the following results were secured:

	Grams.	Grams.
Nitrogen as nitrite reacting material in gas	.001205	
Nitrogen as nitrite reacting material in flour		.00108
Nitrogen as nitrite reacting material in air		.00008
Total		.00116
Mechanical loss and error		.000045

A number of determinations were made, and it was found that up to 25 c. c. of nitric oxide per kilogram of flour, all of the nitrite reacting material in the bleaching gas was accounted for as nitrites in the flour or air, leaving none to chemically unite with the flour to form nitro-compounds. It is to be noted that this is a much larger quantity of bleaching gas than is employed in commercial bleaching by electrical processes.

In the third series of experiments, water was substituted for the flour, in which case less nitrites, but apparently a larger amount of nitrates were obtained.

In these experiments the nitric oxide was prepared by the action of copper upon nitric acid; the gas upon analysis showed a purity of 77 per cent. (For impurities see Watt's Dictionary of Chemistry.) The permanganate method and the method of absorption by ferrous sulphate were employed for the analysis. The gas was absorbed in water, and the amount of nitrite reacting material was determined by the Greiss method. About half of the nitrogen was accounted for as nitrites. As previously stated the gas ordinarily yields nitrates and nitrites in equal amounts. Attempts were made to also determine the nitrate reacting materials, and as noted the methods for the determination of nitrates do not admit of the recovery of the small quantities present in flour as in the case of nitrites. In working with flour it was found that the last traces of soluble carbohydrates could not be removed from the aqueous solutions without oxidation of nitrites or mechanical loss of nitrates. Aluminium cream, lead acetate and all of the usual reagents were used for clarification but without effectual results. Unbleached flours supposed to be nitrite free, were found to react with the reagents, due to soluble carbohydrates, and to produce yellow colored products similar to nitrates.

That the nitrite reacting material is physically absorbed by the flour and is not in chemical combination is further suggested by its behavior when warmed. Commercially bleached flours, as previously stated, lose their nitrite reacting material when heated. In one of the trials, a laboratory over-bleached sample containing .000277 grams nitrite nitrogen per 100 grams of flour, lost 66.3 per cent of its nitrites after four hours heating at a temperature of 85° to 95° C. The flour still contained moisture with which the nitrite material could be associated.

No experiments were made to determine the point at which chemical changes other than bleaching of the pigment might occur. It is evident that these do not take place under commercial conditions of electrical bleaching. That there may be a chemical combination between larger amounts of nitrogen peroxide and flour is doubtless true, but when the gas is present in such small amounts as are used in the bleaching of flour, it appears to act in its well known capacity of "a carrier of atmospheric oxygen," and not as a nitrating reagent.

Laboratory Experiments with Different Quantities of

Bleaching Gas. A series of experiments was made to determine the influence of different amounts of nitrogen peroxide upon flour and the relationship between the amount of bleaching gas used and the nitrites found in the flour. The gas was measured as nitric oxide into a four litre flask, containing 200 grams of flour. This flour, used in all the tests, was milled from hard spring wheat in the experimental mill of the Minnesota Experiment Station and consisted of the middlings and break flours. It was about a 93 per cent patent. The flour was not strictly comparable with that milled in commercial mills because the wheat and flour stock are not as completely cleaned in the smaller experimental mill, owing to lack of cleaning devices. The flour was effectually bleached with one c. c. of gas, that is at the rate of 5 c. c. per kilogram of flour. The bleaching of the flour caused the impurities as bran and cellular products to become blackened and more pronounced. From a commercial point of view the bleaching of this flour which contained the low grades, was not successful.

The experiments noted were conducted with the view of determining mainly the extent to which the nitrites were retained in the flour when different quantities of the gas were used. In ordinary commercial bleaching of flour by the electrical process there remains a nitrite reacting residue at the rate of four-tenths parts per million of flour. This is practically the amount retained when flour is bleached experimentally at the rate of 5 c. c. of gas per kilogram of flour. The nitrites were determined on the fresh flour and also on flour after exposure in sacks for 24 days. The maximum quantity of gas used was 250 c. c. per kilogram of flour, fifty times more than is required for bleaching. It is to be noted that in the case of this excessive amount of gas the nitrite nitrogen in the freshly bleached flour was eight parts per million, but at the end of the 24 days it was four parts per million, the same as when smaller amounts of the gas as 25 c. c. portions were used. Alway (Nebraska Experiment Station Bulletin No. 102) has shown that when excessive amounts of gas are employed, over 200 c. c. per kilogram, the amount of permanent nitrite material remaining in the flour after three or four weeks is no greater than when smaller quantities of gas are employed. It is to be noted that up to fifty c. c. of gas per kilogram of flour, the amount of nitrite reacting material in the flour was proportional to the amount of nitrogen peroxide used and that when larger amounts of gas were employed the quantity of nitrites was not found to increase in the flour after it had been stored three weeks. It is not possible from the determination of the nitrites to detect flours that may have been subjected to excessive or over bleaching like these laboratory samples. It would be inconsistent to claim that a laboratory over-bleached sample had been subjected to the same treatment as a commercially bleached flour because the same amount of nitrite residue is found in each. The extent to which the bleaching has been carried can be determined by the nitrite reacting material only up to a certain point, and beyond that bleaching does not increase the nitrites. In these laboratory tests with over bleached flours, a slight odor could be detected in the fresh samples. There is little danger, however, of flours being bleached to such an extent as to impart an odor, as such a procedure would lower their commercial value. The effect of different quantities of gas upon the amount of nitrite reacting material in the flour is given in the following table:

No.	Flour Grams.	Quantity gas used, c. c.	Time exposed.	Date treated.	Nitrogen as	
					Nitrites per 100 gms. 7/3/08	Nitrites per 100 gms. 7/27/08
1....	200	1	1′	A. M. 7/1/08	.0000422	.000042
2....	200	2	1′	"	.00005	.00005
3....	200	3	1′	"	.0000528	.000052
4....	200	4	1′	"	.000066	.000052
5....	200	5	40″	"	.0001	.0001
6....	200	5	1′	"	.00012	.00007
7....	200	10	1′	"	.000316	.0002
8....	200	15	1′	"	.000316	.00028
9....	200	20	1′	"	.0004	.0004
10....	200	25	1′	"	.0004	.0004
11....	200	1	1′	P. M. 7/1/08	.0000422	.000042
12....	200	2	1′	"	.0000528	.00005
13....	200	3.1	1′	"	.000066	.00005
14....	200	4	1′	"	.0001	.000055
15....	200	5.1	40″	"	.0001	.0001
16....	200	5	1′	"	.00013	.0001
17....	200	10	1′	"	.000316	.00028
18....	200	15	1′	"	.000316	.0004
19....	200	25	1′	"	.0004	.0004
20....	200	25	1′	"	.0004	.0004
21....	200	50	1′	"	.0008	.0004

Loss of Nitrites in Bread Making. Bread made from bleached flours containing .00004 per cent nitrogen as nitrites and baked out of contact with combustion of gases gives no reaction for nitrites. Bread made from unbleached flour and baked in a gas oven in which there is direct connection between the combustion chamber and the oven shows appreciable amounts of nitrites formed from combustion of the gas. It is a well established fact that nitrites are produced when gas, fuel and organic matter in general are burned, in fact water boiled over a gas flame reacts for nitrites. In the baking of bread the amount of nitrites absorbed from combustion of the gas depends entirely upon the construction of the oven. When the oven is provided with a ventilating flue the minimum amount is absorbed and then there remains in the bread only approximately .000001 grams per 100 of nitrite nitrogen. In bread made in the laboratory but little difference was observed between the nitrite content of that from bleached and unbleached flour when both were baked in a gas oven. When the bread was properly made and baked in an electric oven there was no reaction for nitrites from either the bleached or unbleached flours, that is provided the flour itself was free from nitrite and nitrate reacting material except that imparted by the bleaching gas.

In experiments where sodium and potassium nitrite were added to unbleached flour the bread gave a reaction for nitrites showing that the mineral nitrites are not volatilized during the bread making process. For this reason it was concluded that the nitrites of bleached flour are neither sodium nor potassium. When mineral nitrites were added to the flour the amount recovered in the bread was greatly reduced, due undoubtedly to the chemical action upon the nitrites of acetic and carbonic acids formed during fermentation. As shown by Prescott and Johnson in "Qualitative Chemical Analysis" nitrites are liberated by acetic acid. It has been established by a number of investigators that acetic acid is one of the organic acids formed during bread making. (See Jago, "Science and Art of Bread Making.") It has also been shown by Moore

(J. Am. Chem. Society, August, 1904,) that carbon dioxide liberates nitrous acid from its salts. In the process of bread making, about one per cent of carbon dioxide is produced and about .2 per cent of organic acids. (Bulletin 07, Office of Experiment Stations.) Thus it will be seen that because of the chemical action of carbonic and acetic acids no appreciable amount of mineral nitrites could remain in bread, as these reagents formed during bread-making decompose nitrites. In former investigations, Bulletin No. 103, it was shown that nitrates and frequently nitrites are found as normal constituents in wheat when the soil is rich in nitrates and that flours made from such wheats give appreciable reactions for both nitrates and nitrites, in some cases as much nitrite being secured as from bleached flour. Hence it would be inconsistent to claim that all flours giving a nitrite reaction have been bleached. The oxidation of nitrites to nitrates and the reduction of the latter again to nitrites are well known reversible reactions that also must be taken into consideration in dealing with this question. The U. S. Pharmacopoeia states in regard to sodium nitrite: "When exposed to the air the salt deliquesces and is gradually oxidized to sodium nitrate." If this statement be correct, it is apparent that no appreciable amount of sodium nitrite could exist in flour or bread without being converted into nitrate. It is also well known that foods containing nitrates either as natural or added products give appreciable reactions for nitrites. If a small amount of nitrite be mixed with a nitrite-free-flour the flour after a time will give reactions for nitrites. This reduction of nitrates to nitrites in the presence of organic materials is well illustrated in the case of meats where saltpeter or potassium nitrate is employed in their curing. Bigelow, in a review of the literature of meat products in the J. Am. Chem. Society, August, 1906, reports: "It has been shown that when one gram of potassium nitrate is added to 300 grams of meat it is reduced first to nitrites and then to ammonia."

The form, or the definite chemical compound, in which the nitrite reacting material in bleached flour is present is not definitely known. It can not be regarded as a mineral nitrite for the reasons previously given, and then too, for the peroxide gas to unite with the mineral matter of the flour as sodium or potassium would necessitate extended chemical reactions in which these bases would first have to be liberated from the elements with which they are combined. Flour contains an appreciable amount of ammonia reacting material. When the aqueous extract from which proteids have been removed is distilled; a large amount of free ammonia is secured. In former investigations at this station it was shown that in bread-making appreciable amounts of nitrogen as ammonia are liberated and volatilized. A small amount of ammonium nitrite can be produced during the bleaching of flour, and it is reasonable to expect that this compound is formed rather than those that require larger amounts of reagents, and different physical and chemical conditions than exist in flour bleaching. Whether some of the nitrite in bleached flour is in the form of ammonium nitrite can not definitely be determined because the amount is too small to allow its separation and identification. The nitrite in flour in many respects resembles ammonium nitrite, as it is readily volatilized, in fact it is decomposed when a solution of it is warmed. (See Remsen, College Chemistry) When ammonium nitrite is decomposed by heat the products given off are free nitrogen gas and water, and hence a study of the volatile products of ammonium nitrite would fail to detect any nitrite reacting material, as the nitrogen is liberated as a free element and not in combination. When a sample of bleached flour is heated and the products are passed into nitrite-free-flour no reaction for nitrites is obtained when this flour is tested, and the bleached flour itself gives no reaction for nitrites. If a small amount of ammonium nitrite is added to an unbleached flour and heated, it behaves in the same way, and neither the flour nor the products give any reaction for nitrites. Because of this similarity between the nitrite reacting material of flour and ammonium nitrite and the fact that ammonium reacting products are present in the flour, it is more reasonable to assume that the nitrite of bleached flour is ammonium nitrite and not sodium or potassium. Ammonium nitrite is present as a normal constituent of the air and is one of the products formed during electrical discharges, and the combustion of fuel. The nitrite of bleached flour is either ammonium nitrite or a volatile compound of similar properties.

Influence of Bleaching of Flour upon the Digestibility of Bread. In order to determine the influence which commercially bleached flour may exert upon the digestibility of bread a series of digestion experiments was undertaken to determine the digestibility of bread made from bleached and unbleached flour milled from the same wheat. This experiment was performed in co-operation with the U. S. Dept. of Agriculture; Office of Experiment Stations, as noted in the annual report of the Director of the Office of Experiment Stations for 1907. Only a summary of these results is here given. In all, 15 digestion experiments with men were made. The ration consisted of bread and milk and the general plan of the experiments was as follows. Samples of bleached and unbleached flours and of the wheat from which the flours were made were drawn from a large commercial mill. Digestion experiments were made with bread baked from the bleached and the unbleached flours. Some of the wheat was then milled in the experimental mill of the Minnesota Experiment Station. One half of the flour was bleached and digestion experiments were made with bread from this bleached and unbleached flour prepared under chemical control. It was found that bread baked in an oven heated with gas generated from gasoline vapor gave reactions for nitrites equal to those obtained from the bleached flours and that bread from both the bleached and unbleached flours when baked in a stove heated by coal, gave no reaction for nitrites. The results of these five series of digestion experiments are given in the following table:

DIGESTIBILITY OF NUTRIENTS.

	Protein Per cent.	Carbohydrates Per cent.	Available Calories
Trial I. Bread from Bleached Flour.			
Man 1	85.74	96.96	91.67
Man 2	84.53	97.52	90.62
Man 3	84.96	97.28	90.35
Average	85.08	97.25	90.88
Trial II. Bread from Unbleached Flour.			
Man 1	86.97	98.47	91.46
Man 2	87.93	98.14	90.89
Man 3	87.63	98.28	91.35
Average	87.51	98.29	91.23
Trial III. Bread from Unbleached Flour.			
Man 1	91.76	99.02	93.87
Man 2	92.14	98.08	94.97
Man 3	91.67	99.08	95.09
Average	91.86	98.73	94.64
Trial IV. Bread made from Bleached Flour.			
Man 1	92.04	99.07	94.41
Man 2	93.24	98.89	95.49
Man 3	93.00	98.88	95.66
Average	92.76	98.95	95.19
Trial V. Bread from Unbleached Flour with Nitrites.			
Man 1	93.56	99.14	95.21
Man 2	93.98	99.19	95.76
Man 3	95.96	99.18	
Average	94.50	99.17	95.43

In one of the trials or series, the nutrients of the bread made from the unbleached flour was found to have a slightly higher digestibility than the bread made from the same flour that had been bleached, while in another series the bread from the bleached flour was somewhat more completely digested. The difference in digestibility of the nutrients of the breads made from the bleached and unbleached flours was too small to be attributed to the treatment the flour had received. The average of the two series shows the bread made from both the bleached and the unbleached flours to have the same degree of digestibility, and that the process of bleaching had no influence upon the digestibility or nutritive quality of the flour. The bread for these experiments was made in an ordinary cook stove heated by coal, and all the products of combustion of the fuel were excluded from the baking chamber. The bread both from the bleached and the unbleached flour gave no reaction for nitrites, the nitrous acid products formed during the bleaching of the flour and present to the extent of .00004 grams of nitrogen determined as nitrites per 100 grams of flour, being entirely expelled during the process of baking.

In the digestion trials with bread made from unbleached flour but baked in a gas oven and that poorly constructed so the products of combustion from the gas found their way into the oven and were absorbed by the bread, the digestibility of the bread was not lowered because of the presence of nitrites to the extent of .00005 grams of nitrogen as nitrites per 100 grams of bread. When this experiment was performed the weather was very severe, and it is believed that the apparent increase in digestibility was due to the greater demand upon the body for heat and energy and this was an important factor in causing more complete combustion of the nutrients. It is safe to conclude from the results obtained that the nitrites present in the bread and which were derived from the combustion of the gas used in baking exerted no unfavorable influence upon the digestibility of the nutrients.

Briefly stated, when flour is bleached by the electrical process a very small amount of nitrite yielding products is formed. When baked into bread, out of contact with fuel gases, these nitrite products were volatilized and the bread gave no reaction for nitrites. When bread was made from unbleached flour and baked in a gas oven connected with the combustion chamber, the bread absorbed nitrites from the products given off in the fuel gases. The nitrites present in the bread made under such conditions did not appear to exert any unfavorable influence upon digestion.

Digestion Experiments with Pepsin Solution. Digestion trials were made with bleached and unbleached flours in acid pepsin solution. The flours used contained 2.04 per cent nitrogen. The insoluble nitrogen obtained after digestion with pepsin was found to be as follows:

Trial No.	Bleached Flour Per cent.	Unbleached Flour Per cent.
1	.392	.378
2	.343	.356
Average	.367	.367

It is to be noted that the differences between the duplicate trials of the same sample are as great as between the two samples of flour tested.

As far as digestibility in the acid pepsin solution was concerned no difference whatever was found in the digestibility of the bleached and the unbleached flours.

Are Flours Bleached with Minute Amounts of Nitrogen Peroxide Injurious to Health? This is a question that can well be raised because if the bleaching leaves any material in the bread that is injurious to health the practice should be discontinued and condemned. The form in which the flour is consumed as food, or the finished food product, is what should be considered in answering this question. Flour is never eaten in the raw state, but in the process of bread-making, cake-making and indeed in all the various ways it is prepared for food it is always subjected to the action of heat. As previously stated when flour is warmed out of contact with combustion gases the nitrite reacting material imparted during bleaching is removed and the bread and other articles made from the flour give no reaction for nitrites imparted by the bleaching gas. Since the material used in the bleaching of flour is expelled in the preparation of the food, there remains no question for physiological consideration. But since breads made from bleached and unbleached flour give practically like amounts of nitrite reacting material when baked in gas, gasoline or kerosene ovens it would seem that the broader question could well be raised: is the use of gas and liquid fuels for the preparation of foods, where the food comes in direct contact with the products of combustion injurious to health? However, this question of the wholesomeness or unwholesomeness of a food is one for the physiologist and the hygienist rather than the chemist to decide. The chemist can determine the amount of a substance in a food material, but from chemical data alone he is unable to determine whether or not this material is injurious. The chemist simply supplies the data from which the physiologist and the hygienist reach conclusions. The presence of nitrites in food materials in general can well be considered in this connection. Nitrites are widely distributed in nature as will be seen from the following quotation:

"*Nitrous Acid,* HNO_2 or $O{=}N{-}OH$. Occurrence.—As ammonium nitrite, $NH_4{-}NO_2$ to a trivial extent in the air, in rain-water, in many spring-waters; it is also formed to a slight extent on the evaporation of water in the air, by the action of the electric spark upon moist air (in rain after thunder-storms), in all combustion processes in the air, and in the slow oxidation of phosphorus in the air, on rusting of iron, and in the electrolysis of water containing air: $2N+2H_2O=NH_4{-}NO_2$. It occurs as nitrites in many plant juices, nasal mucus and saliva."—(Compendium of Chemistry. Arnold. Mandel.)

Air is one of the most important of food materials. In order to determine the extent to which nitrites are formed during combustion of kerosene, gas and gasoline, a series of experiments was undertaken in which the air in rooms where these were burned was analyzed.

Experiment No. 1. *Outdoor Air.* Air was collected from the top of a hill, the highest point on the campus. At the time the wind was blowing from the northwest over farm land. About 100 cubic feet of air were metered through absorption bottles and a reaction was secured for traces of nitrites. On a rainy day from the same locality 33 feet of air gave a decided reaction for nitrites.

Experiment No. 2. *Air from a Dwelling House.* The doors and windows of a room 15½x10½ feet with an open closet 3½x7 feet, were closed and a student's lamp was left burning in the room for half an hour before the beginning of the experiment. Then 15 cubic feet of air were metered through absorption bottles during 2½ hours and .000004 grams of nitrogen as nitrites were secured. Five ounces of oil were burned. The room was provided with some ventilation, through a register which was open to pass the tube for connection with the suction pump, and a ventilator extending from the floor to a ventilating flue in the chimney. The experiment was repeated with gas burned in the same room under similar conditions and for the same length of time, when 15 cubic feet of air yielded .0000044 grams of nitrogen as nitrites.

Experiment No. 3. *Kitchen Air.* Size of room, 16x10 feet. One gas stove burner was lit at the beginning of the experiment, also the gas range burner for warming water, but this burner was provided with a ventilating pipe connected with the chimney. Ten cubic feet of air were drawn through the absorption bottles in one hour and a half and .000028 grams of nitrogen as nitrites were secured.

Experiment No. 4. *Office Air.* Size of room, 18x21x10 feet. The windows were closed, but two ventilators connecting directly with outside air were open. One gas light was burned for three hours. The gas was produced from gasoline. Thirty-eight cubic feet of gas yielded .0000085 grams of nitrite nitrogen. The experiment was repeated with a student's lamp burning for 1½ hours, when 15 cubic feet of the air yielded .0000033 grams of nitrite nitrogen; 3½ ounces of oil were burned. In the case of a second lamp with 1¼ inch wick burning 2½ ounces of oil in three hours, 40 cubic feet of air yielded .000006 grams of nitrite nitrogen. At the beginning of all of the experiments the doors and windows of the rooms were opened and the rooms were thoroughly aired.

Experiment No. 5. Bake Room Air. Two windows and one door of a baking room were open and the equivalent of about six gas burners were being used, when 20 cubic feet of air yielded .000005 grams of nitrite nitrogen. With the room closed, but other conditions the same, 10 cubic feet of air yielded .000044 grams of nitrite nitrogen. Six cubic feet of air drawn from the bake oven while the gas was burning yielded .00001 grams of nitrite nitrogen. 500 c. c. of nitrite free water were placed in the bake oven for 30 minutes and the gas was lighted. At the end of that time 100 c. c. of the water tested .00005 grams nitrite nitrogen.

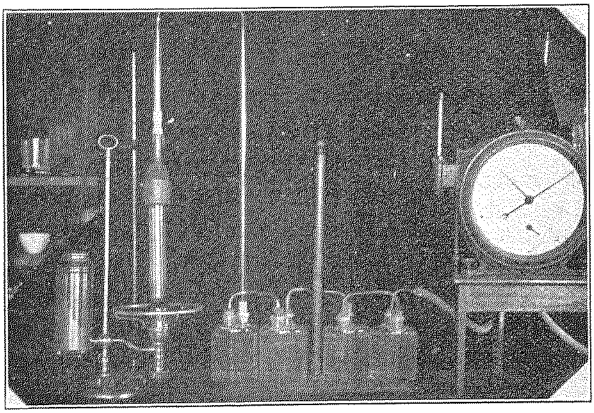

Fig. 2.—Apparatus used in collecting nitrites produced by a lamp.

Experiment No. 6. Nitrite Collected Directly from a Lamp. The chimney of a student's lamp was connected with an iron pipe and the products of combustion were aspirated directly into absorption bottles. In ten minutes

.000045 grams of nitrite nitrogen were collected. From this and similar experiments it was estimated that a student's lamp gives off .00027 grams of nitrite nitrogen per hour.

Experiment No. 7. Twenty-four Hour Test with Lamp Burning Five Hours in Room. In all of the preceding tests the experiments were conducted for periods not exceeding three hours. In northern latitudes it not infrequently happens during winter months that a lamp is burned five hours of the twenty-four, the room receiving but little ventilation and the larger portion of the nitrites produced from the combustion of the oil being retained in the room. A lamp was burned for five hours in a room provided with ventilation, when 32 cubic feet of air yielded .0000055 grams of nitrite nitrogen. Then during a second period of eight hours after the lamp had been extinguished, 48 cubic feet of air yielded .0000106 grams of nitrite nitrogen. It is to be noted that in the second period there was more nitrite proportionally than in the first period, due to the nitrites having accumulated through combustion of the oil and being retained in the room. During a third period of 11 hours, 66 cubic feet of air yielded .0000131 grams of nitrite nitrogen. During the 24 hours' test 146 cubic feet of air drawn from the room yielded .0000292 grams of nitrite nitrogen.

From these experiments it is evident that, under ordinary conditions of life, nitrites are taken into the system through the air that is breathed. Dr. Howell, of Johns Hopkins University, estimates that a person at rest will breathe about 380 cubic feet of air per day. If a person spend five hours in a ventilated room where a lamp is burning and then sleep eight hours in the same room where the nitrites have accumulated and remain in the room three hours additional during the day—leaving eight hours to be spent out of doors—he will inhale over .00005 grams of nitrite nitrogen. In cases where food is cooked with gas, gasoline or kerosene, and bread is baked, clothes are ironed or cooking processes are carried on for several hours, as is frequently the case, the amount of nitrite reacting material inhaled is greatly increased. From the experiments taken as a whole, it will be seen that not infrequently a person inhales during a day more nitrites than are present in a pound of bleached flour in the raw state before the nitrites are volatilized by baking, and it is seldom, if ever, that flour is eaten in this condition.

The nitrites in drinking water often add materially to the amount consumed per day under average conditions. Rain water contains about one part per million of nitrite nitrogen and even distilled water generally gives reactions for appreciable amounts. In ham, bacon, and salted and preserved meats there are ten parts or more of nitrite nitrogen per million, or over ten times more than is in average bleached flour. Meats that are preserved with smoke without the use of saltpeter also give reactions for nitrites. Wood smoke contains nitrites as products of combustion. The preservation of foods by the use of smoke is sanctioned by practically all food authorities, and meats prepared with "common salt, sugar, wood smoke, vinegar, pure spices" are exempted under the provisions of the national food law. (See Circular No. 39, Meat Inspection.) If flour be submitted to wood smoke for only a few minutes, it shows as large a content of nitrites as when bleached and the smoked-flour would not be considered injurious to health. During the process of smoking, meats come in contact not only with nitrites, but also carbon monoxide produced from the smouldering of the wood, which is one of the most poisonous gases known, but it would be inconsistent to claim that smoked meats are injurious to health because they have been brought in contact with carbon monoxide or nitrites during the process of smoking as neither undergoes fixation.

Nitrites are known to be present as natural constituents in many food products, particularly those of vegetable origin, as celery, lettuce and beets in the early stages of growth. It not infrequently happens that the nitrite content of fresh vegetables reaches the third or fourth decimal place. Both nitrites and nitrates have been found by the author in milk where cows have been fed liberally on beets. The presence of nitrates in milk under similar conditions has been reported by Richmond and others. Nitrites are also present as a normal constituent of the saliva.

NITRITES IN MISCELLANEOUS FOODS.

	Nitrogen as nitrites per 100 grams material.
Bread—	
Made from unbleached flour, flour ground in laboratory experimental mill from wheat grown on University Farm	
Fertilized with nitrogen	.000006
Fertilized with potash	.000009
Fertilized with phosphate	trace
Made from unbleached flour, flour ground in laboratory experimental mill from wheat grown in different parts of state where fertilizer tests had been made:	
Sample A. Fertilized with nitrogen	.0000064
Sample B. Fertilized with phosphates	trace
Sample C. Fertilized with potash	none
Sample D. Complete fertilizer	trace
Sample E. No fertilizer	none
Sample F. Fertilized with phosphates	none
Dried Beef	.0002
Bacon	.0004
Ham	.0005
Oysters	trace
Sugar	trace
Smoked flour	.00005
Water boiled half hour over gas flame in open dish	.00003
Milk from cow fed liberally on beets	trace
Grapes	trace
Shredded wheat biscuit	.000004
White of egg	trace
Ham, smoked, no saltpeter used (ham cured at station)	.00005
Water, boiled in tea kettle and cooled (high grade water from sanitary point of view)	trace
Salt	.000001
28 Samples Macaroni Wheat—	
7 samples	no reaction
3 samples	trace
18 samples	.00001 to .000003
Bread made from commercial flour known to be unbleached (bread baked in gas oven, oven well ventilated)	.000002
Ditto, baked in oven of wood stove	.000002
Rain water	.00009
Charcoal used for medicinal purposes	.000005
Oatmeal	trace
Crackers	.00001

Small amounts of nitrites in drinking water are not generally regarded as injurious by hygienists unless the nitrites are associated with objectionable bacteria. The nitrites alone are inocuous, as stated by Sutton, "Volumetric Analysis," page 500. Even if the nitrites in bleached flour were not removed during bread making, or the flour were eaten in a raw state the amount consumed would be insignificant. As previously stated it is not known in what form the nitrite reacting material is present. Assuming it is sodium, Alway has calculated that it would be necessary for a person to eat a pound loaf daily to obtain the equivalent of "a medicinal dose of nitrites in the course of a year." And "whether there will be any nitrites at all in the bread depends, as has been stated, upon the method of making it." Similar results would be reached in basing the calculations on the nitrite content of the flour samples reported in this bulletin.

From the facts taken as a whole it is quite evident the bleaching of flour with traces of nitrogen peroxide could in no way impart enough nitrites to render the flour or the products made from it injurious to health or to make their use as food even questionable.

Use of Chemicals in Preparation of Foods. The principle of the use of chemical reagents in the manufacture and refining of foods is recognized in the rules and regulations for the enforcement of the national food and drugs act. Circular No. 21, U. S. Department of Agriculture, Office of the Secretary, Regulation No. 11, states: "Substances properly used in the preparation of food products for clarifying or refining and eliminated in further process of manufacture" are exempt. There is no substance or material used in the manufacture of food products that is as completely eliminated from the finished product (bread) as is the nitrogen peroxide and its products, used in the bleaching or refining of flour. In the manufacture of sugar, sulphur in the form of sulphur dioxide gas is used for bleaching purposes. Lime is employed later in the process for neutralizing the sulphurous and sulphuric acids formed and for producing insoluble products which are later removed by filtration. The last traces of the sulphur, however, are not entirely removed, and careful analysis of commercial samples of granulated sugar after combustion in a calorimeter have shown .0098 per cent of total sulphur. On a percentage basis this is nearly fifty times more than the total nitrate and nitrite products retained in flour, bleached by the use of nitrogen peroxide. Furthermore sugar is used directly as food without any of the sulphur being volatilized. Notwithstanding the presence of this trace of sulphur, granulated sugar is practically pure, as it is unacted upon by the sulphur. The sulphur acts only upon the coloring matter and not upon the sugar. However, a much larger amount of it is used than of nitrogen peroxide in the bleaching of flour. With large amounts of sulphurous and sulphuric acid, chemical reaction takes place with sugar, but the little used as a bleaching reagent fails to produce such a change. In the same way the small amount of nitrogen peroxide used in flour bleaching acts upon the coloring matter of the flour without uniting with any of its constituents. A large amount of gas, however, would produce chemical changes as would a large amount of sulphur dioxide acting upon granulated sugar. Sugar is a food consisting of only one nutrient. In order to refine and improve it the coloring matter is removed by bleaching. This bleaching is done without affecting the composition. Flour is a food consisting of several nutrients and the coloring material is bleached by a trace of nitrogen peroxide, without otherwise affecting the composition.

Influence of Bleaching upon the Bread-making Value of Flour. A large number of bread-making experiments with bleached and unbleached flours milled from the same wheat have been made in this laboratory. When the flours were milled and bleached in the laboratory and the bleaching reagent, nitrogen peroxide, generated by electrical action from the union of nitrogen and oxygen of the air, there was a slight tendency for improvement in bread-making value. In all of the tests where nitrogen peroxide generated by chemical action was used at the rate of less than 150 c. c. of gas per kilogram of flour, bleaching had no injurious effect upon the quality of the bread. When the electrical machine was operated to its full capacity and the flours were left in contact with the bleaching medium for five minutes or longer no injurious effects were observed.

Bread from bleached flour (flour bleached in laboratory)—	Volume of loaf c. c.	Weight of loaf. grams.
1st baking	1410	360
2nd baking	1420	362
3rd baking	1405	360
Bread from same flour, unbleached—		
1st baking	1400	358
2nd baking	1418	361
3rd baking	1412	360

Testing Commercial Samples of Bleached Flour. In order to determine the extent to which electrical bleaching of flour as practiced by the millers of the state affects the bread-making value, a circular letter was sent to twenty-three mills asking for samples of bleached and unbleached flour milled from the same wheat. Sixteen of the mills, representing a total daily capacity of 120,000 barrels of flour, responded and furnished samples. The letter said: "In order that no advantage may be taken by anyone for advertising purposes, claiming the flour from one mill superior to that of another, the samples will be referred to by number, and the only comparisons will be between the bleached and unbleached flour furnished by each mill." In all cases the bleached and unbleached flours were found to be practically identical in ash content, showing that the samples had been accurately taken and were identical except as to bleaching. In one case samples sent as unbleached proved to be bleached.

The bread from these flours was made under uniform and similar conditions by one of the assistants in the laboratory, who is an experienced bread-maker, having had charge of the testing room of a large flour mill. The only way in which the bread-making value of a flour can be determined is by comparative tests in which a flour of known bread-making value is used as a standard. It is not possible from the baking of a bleached flour alone to determine the influence of bleaching, unless a sample of the same flour unbleached is used for comparison, and the breads are made at the same time and under similar conditions. It is necessary that all factors except the one in question—bleaching—be alike. Poor bread may be due to a number of causes, as poor wheat, inferior milling, damage while in transit, poor yeast or lack of skill on the part of the bread maker.

Flour No.	Bleached or Unbleached.	Nitrogen as nitrites in 100 gms. flour.	Volume of loaf, c. c.	Dimensions of loaf, inches.
1	Bleached	.00007	1425	16⅞x21¾
2	Unbleached	slight trace	1410	16½x21½
*3	Bleached	.0000278	1440	16¾x21¼
4	Unbleached	.0000278	1360	15⅝x20⅞
5	Bleached	.000033	1410	16⅛x21⅛
6	Unbleached	none	1325	15⅛x20⅜
7	Bleached	.000035	1425	15⅝x20¾
8	Unbleached	trace	1355	15¾x21
9	Bleached	.000033	1405	15⅞x20¾
10	Unbleached	.000003	1435	16 x20¾
11	Bleached	.000056	1460	16⅜x21
12	Unbleached	none	1335	15¾x20½
13	Bleached	.00005	1465	16½x21½
14	Unbleached	.000008	1460	16⅜x21¼
15	Bleached	.000086	1450	16 x21
16	Unbleached	trace	1410	16¼x21¼
17	Bleached	.00006	1485	16¼x21⅜
18	Unbleached	.000007	1450	16⅛x20⅞
19	Bleached	.0000278	1420	15⅞x21⅛
20	Unbleached	none	1435	16¼x21⅛
21	Bleached	.00002	1445	16⅜x21⅛
22	Unbleached	none	1440	16½x21¼
23	Bleached	.000035	1465	15⅝x20⅝
24	Unbleached	none	1480	16½x21⅜
25	Bleached	.00002	1455	15⅜x20⅜
26	Unbleached	trace	1525	16⅜x21½
27	Bleached	.0000278	1475	16⅛x20⅞
28	Unbleached	trace	1455	15⅞x20⅞
29	Bleached	.000102	1450	15⅝x20⅜
30	Unbleached	none	1400	15½x20½
31	Bleached	.00005		
32	Unbleached	trace	1460	16¼x21¼
			1440	16 x21⅛
Av. volume of loaves: bleached..			1446	
unbleached			1449	

*Omitted from average.

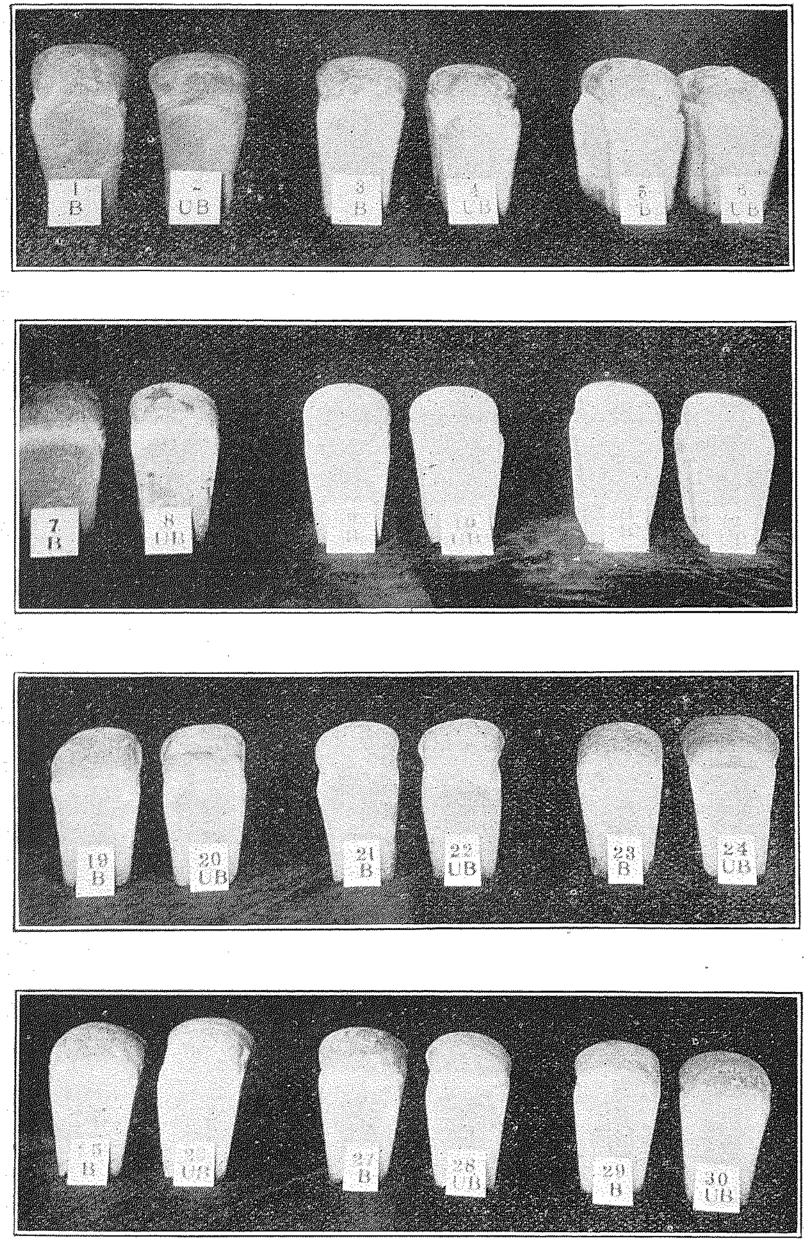

Fig. 3.—Breads made from Commercial sample of bleached and unbleached flours. B—bleached. UB—unbleached

In the table it will be noted that in the case of six of the pairs of loaves made from bleached and unbleached flours there was no greater difference in volume (25 c. c.) than between duplicate bakings of the same flour. In eight of the fifteen pairs the bread made from the bleached flour exceeded in volume that from the unbleached by more than 25 c. c. It is believed this was largely due to the bleached flour being somewhat drier and hence in the bread-making tests the 248.6 grams of bleached flour contained a little more dry matter than the same weight of unbleached flour. In one case the bleached flour produced the smaller loaf. In all of the tests the bread from the bleached flour was whiter. All the flours produced bread of good odor and taste. There was no difference in the odor of the breads made from the bleached and the unbleached flours, in fact the breads were similar in all respects except in color and general tendency of the bleached flours to produce a larger loaf. No tests were made to determine the influence of excessive amounts of nitrogen peroxide upon the bread-making value of flour as such experiments would not be in accord with commercial conditions. That a large amount of nitrogen peroxide, sufficient to impart taste and odor and affect the bread-making qualities can be added to flour is undoubtedly true, but in commercial bleaching where the nitrogen peroxide is produced from the air in traces by electrical action, this does not take place as the quantity of gas generated is insufficient to produce such results. As far as quality of the bread is concerned it is in no way impaired by bleaching of the flour. In fact, it produced a whiter bread which is more pleasing in appearance to many; and because of the drying action it has a tendency to produce larger sized loaves.

From a pecuniary point of view the bleaching of flour has a tendency to be beneficial to the consumer as the flour is weighed at the mill after it has been bleached and a small amount of moisture thus removed. This results in the consumer receiving a larger amunt of dry matter as well as a whiter flour. The process is beneficial to the miller as it enables him to place his flour directly upon the market without its having to undergo the natural curing and aging process by storage during which bleaching takes place. To the miller the expense of bleaching and any loss in weight incident to drying are compensated for by securing immediately flour that is cured and ready for the market, thus saving the interest incident to the flour undergoing natural curing in storage. Flours bleached with small amounts of nitrogen peroxide generated by electrical action are in all respects similar to flours bleached and cured by storage except that the electrically bleached flours contain a trace of nitrite reacting material which is removed during the process of bread-making.

Bleaching of Low Grade Flours. In the process of milling about 75 per cent of the cleaned wheat is recovered as flour and 25 per cent as offals; about 72 per cent is high grade, and two to three per cent low grade, the larger portion of which is "red dog" generally used for feeding animals. The classification of flour into patents, straight or standard patent and low grade is purely arbitrary and in no two milling systems are the separations identical, that is, one mill may produce a flour, a larger amount of which is returned as patent than another mill, depending upon the grade of wheat and the system of milling. Milling is purely a mechanical process and by a more complete removal of the bran, germ and cellular particles, a larger per cent of the flour is secured as high grade. It is not possible to refine the lower grades without removing the impurities, and when this is done, the flour is of higher grade. As previously stated the bleaching of low grade flour imperfectly milled and containing a large amount of cellular matter, results in discoloration or darkening of the impurities while the flour particles are bleached, the difference between the flour and its impurities being intensified. For this reason, as pointed out by Fleurent and others (see Minn. Exp. Station Bulletin 85, page 27), bleaching is not applicable to low grades or flours that are not thoroughly cleaned and well milled, as the bleaching simply tends to make more pronounced the impurities. Hence it is not possible as has been suggested, for any fraud to be practiced by means of bleaching low grades so as to blend them with patents. Various attempts have been made to commercially bleach low grade flours, but none of these have been successful. [Credit is due Messrs. A. D. Wilhoit and Wm. H. Frazier for assistance in analytical work rendered in this investigation.]

SUMMARY.

1. The bleaching of flour is a natural process and takes place when flour manufactured from well cleaned wheat is stored in thoroughly ventilated warehouses. With natural aging and bleaching there is a slight improvement in bread-making value.
2. The coloring matter of flour is an unstable organic compound readily acted upon by heat, light, air and a number of chemical reagents. It is mechanically associated with the fat and gluten as an impurity.
3. The coloring matter of flour is acted upon by a number of chemical reagents as chlorine, sulphur dioxide and traces of nitrogen peroxide.
4. None of the methods proposed for flour bleaching except the use of minute amounts of nitrogen peroxide as that generated by the discharge of electricity in the air, have survived the experimental stage.
5. 100,000 parts of air containing from four to eight parts of nitrogen peroxide will effectually bleach flour and there is left in the flour, nitrogen as nitrite reacting material amounting to less than one part per million of flour.
6. The fat from bleached and unbleached flour milled from the same wheat is identical as far as iodine absorption number, nitrogen content and heat of combustion are concerned, no greater differences being observed between the fat from the two flours than in the case of duplicate determinations on the same sample.
7. The glutens from the bleached and unbleached flours are identical in physical properties and show the same index of refraction.

8. The nitrogen peroxide used in small amounts in the electrical bleaching of flour exerts no chemical action upon the flour other than upon the coloring matter. The nitrogen peroxide appears to act in its well known capacity of carrier of atmospheric oxygen, taking up oxygen from the air, oxidizing the coloring matter and again taking up oxygen from the air without itself entering into the chemical composition of the flour .

9. The nitrite reacting material in flour appears to be in physical rather than chemical combination. When the flour is heated, the nitrite reacting material imparted by bleaching is expelled. All of the nitrite reacting material in the gas employed for bleaching can be accounted for as soluble and volatile nitrites in the flour and in the air surrounding the flour, leaving no nitrite reacting material to chemically combine with the fat or gluten. When the bleaching gas was brought in contact with pure sand, with which it cannot unite chemically, the same amounts of nitrites were absorbed as in the case of flour.

10. In tests where different quantities of gas were used it was found that the amount of nitrite reacting material left in the flour increased with the amount of gas used up to a certain point and that when a large excess of the gas was employed there was permanently retained in the flour no more than when less of the gas was used.

11. It was found that no relationship whatever existed between the nitrite reacting material in the flour and in the bread. Breads from both bleached and unbleached flours when baked in a gas oven where there was poor ventilation contained the same amount of nitrites. When the breads were properly made and baked out of contact with the combustion gases no reaction was secured for nitrites. Bread can not contain any appreciable amount of nitrite reacting material as the carbon dioxide and organic acids produced during bread-making liberate nitrites.

12. In fifteen digestion experiments with men no difference whatever was observed in the digestibility of breads from bleached and unbleached flour. The bleaching of the flour exerted no influence whatever upon the

amount of nutrients absorbed and digested. Artificial digestion experiments with pepsin solution gave similar results.

13. A kerosene lamp will produce in one hour .00027 grams of nitrite nitrogen. This is over five times more than is present in a pound of an average sample of commercially bleached flour. Nitrites are produced as a result of combustion of all fuels and organic substances containing nitrogen. Flour exposed to wood smoke for a few minutes will contain more nitrites than when electrically bleached. Foods prepared by recognized and approved methods, as smoking of meats, contain nitrites. Salted, smoked and cured bacon, hams and similar meats, contain much larger amounts of nitrites than bleached flour.

14. Nitrites are present in traces in air and in large amounts in ventilated living rooms where gas or kerosene is burned. Nitrites are constituents of rain water, of many drinking waters, and of vegetable foods in the earlier stages of growth as celery, lettuce and spinach. Nitrites are also occasionally found naturally in wheat. They are a normal constituent of saliva and with nitrates are often found in milk where the cows have been fed liberally on roots.

15. The use of chemical reagents in the preparation of foods is recognized where the material is employed for refining and is subsequently removed in the process of manufacture as in the case of sugar, where the coloring matter is acted upon by sulphur fumes and the sulphurous and sulphuric acid products are later removed by precipitation. As a result of the bleaching of sugar, and recognized as an essential part of the process, a larger quantity of the residue from the bleaching gas is permanently retained than is the case in the bleaching of flour. The nitrogen peroxide used in the bleaching of flour is more completely removed in the finished food product (bread) than is any other reagent employed in the manufacture or refining of foods.

16. In bread-making tests of commercially bleached flours no difference whatever was observed between the breads produced from the bleached and the unbleached flours milled from the same wheats except that the bleachd flours produced a whiter bread and also showed a

tendency to produce larger sized loaves. Bleaching of the flour did not impart any odor or taste to the bread or leave in it any residue.

17. The bleaching of flour enables the miller to manufacture a more uniform product and to place his flour directly on the market without necessitating its undergoing bleaching and curing in storage. No difference whatever was observed between the naturally bleached flours and those bleached by the electrical process except that the latter contained traces of nitrite reacting materials which were expelled during bread-making.

18. The bleaching of flour has a slight drying effect resulting in the consumer receiving a proportionally larger amount of dry matter in the flour.