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The Significance of the Browning Reaction in Processed Foods

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Introduction

A discussion of the application of the results of browning research to food products must be very largely an attempt to resurvey old information and to organize it as clearly and logically as possible in terms of a newer terminology. This is not a simple task, for the vantage ground on which one stands to survey the area is none too firm. The term "browning" itself loses sharpness when it comes to estimating the significance of the reactions in food preparations. Processing and storage changes may bring about such desirable results as improvements in color, flavor, and texture, or such undesirable effects as quality deterioration in the same properties. Browning may be involved in both instances. One thus has a term somewhat comparable to "an honest thief."

The major interest of processed food distributors in the domestic market is in processing changes, since duration of storage is usually short, and storage conditions such that "shelf" losses can be largely avoided. Almost any items to which heat is applied in processing serve as examples of products that become unacceptable in appearance, texture, and flavor on long storage. There are a few exceptions to the rapid turn-over practice. Dried apricots and apples, which require holding until the next crop becomes available, i.e., about one year, are examples.

Cereals stored as grain seem to be reasonably stable. There is evidence for believing that long-time storage changes in functional properties and biological values of cereals may not be entirely attributable to enzyme action, and that it is likely that browning reactions are significant in this connection. Jones and associates (1) have reported the results of studies on the proteins of wheat and corn which had been stored up to two years. Decreases in protein digestibility and nutritive values were observed. Products of enzymic action are known to be present in media containing water near the optimum concentration for browning and it is reasonable to believe that these products contribute to browning.

Food processed for use by the Armed Forces in time of war presents the same problems as those involved in processing for civilian consumption, but in a considerably intensified form. For examples, the "pipelines" from processors to consumers - who may be half the world apart - are such that storage life requirements may be greatly extended. Eighteen months, or even two years, may lapse between the processing and packaging of foods and their consumption. Mixtures of items in the same container, not usual in civilian markets, are in some instances desirable or even mandatory in packaged rations intended for military feeding. Transportation and storage conditions may be most unfavorable, involving exposures to high temperatures aboard ship or in desert stock piles. There are also areas of high humidities, extreme cold, etc., to be considered. The results of these processing and storage changes, probably often initiated by processing, are reflected in lowered acceptance, changed functional properties, and altered nutritional values. Development of toxic products is also a possibility.

The acceptability of food preparations may be lowered to the point of rejection by the appearance of disagreeable colors attributable to browning; this is probably due in part to a lack of appeal to the esthetic sense, a response sometimes observed in evaluating the acceptability of fruits and dried soup preparations. Lowered acceptance may also be ascribable to the development of off-flavors, such as those which may appear in citrus juices, dried whole eggs, and dried milk. Finally, unfavorable changes in texture can likewise, in some instances, be attributed to browning. Dried whole eggs, when used for scrambling or in custards, represent a reasonably well established example of these texture changes, and it is probable that difficulties encountered in reconstituting dried whole milk can likewise be charged to similar changes.

It is possible that the demand for a variety of foods is a phase of acceptance. The complaint of monotony of diet was widely prevalent among military personnel forced to make food selections from processed items stored for long periods. The feeling of monotony may arise from any one of a number of causes - as an expression of food habits, from nutritional inadequacy of the rations, or perhaps from the formation of appetite depressants. Of interest in this connection is a University of California investigation (2) on the nutritive value of browned apricots wherein chicks were fed the deteriorated fruit. Although no impairment of the nutritional value of the apricots was observed, food intake was decreased by inclusion of the browned fruit. As the authors point out, the reduced food intake may be due to destruction of an unknown factor, marginal in quantity in apricots, or to the formation of deleterious substances. Now that a beginning is being made in the chemical identification and characterization of browning complexes, it would seem very much worthwhile to explore the relation of these compounds to appetite and satiety.

That browning may cause changes in functional properties, probably closely related to texture changes, is well established in the loss of aerating power of stored dried egg white which has been permitted to retain its small quantity of reducing sugar. It may be reasonably assumed that loss of redispersibility of milk powders and lowered baking properties of long-stored cereal flours may in some way be associated with browning.

Heat and prolonged storage affect the nutritive values of many food proteins as shown by numerous experiments on laboratory animals and humans. The effects of heat may be favorable or unfavorable. Favorable effects appear to be attributable to denaturation of proteins or to the heat inactivation of antitryptic agents. Unfavorable effects appear to be due to changes that, in part, fall into the group of browning reactions. Two possible explanations of the decreased nutritive values of proteins have been advanced. First, that postulated by Block, et al (3) which conceives of a reaction between the free carboxyl groups of the dicarboxylic acids and the free amino group of lysine. There is evidence that such linkages are not hydrolyzed by in vitro enzymic action, but the lysine is made biologically available, as measured by microbial growth, after acid hydrolysis. This type of reaction is believed to be outside the scope of this discussion. The other type, involving carbohydrates as well as proteins, appears to be a likely typical browning reaction. At the present state of research it is difficult to differentiate between the two reactions. Autoclaving proteins, as those of soya, may result in lowered biological values which may be largely restored by hydrolysis. Autoclaved soy meals, or soy proteins, plus sucrose - the resulting monosaccharides - do not yield biologically (Leuconostoc mesenteroides) available lysine after acid hydrolysis (4). Lysine autoclaved with cerelose is unavailable for chick growth (5).

It is interesting to note that Benedict and collaborators, in a series of studies (1918-1922) on the reducing substances which regularly appear in urine of normal humans, reached the conclusion that the excretion of "sugar" is intimately related to ingestion of food. Folin and Berglund (6) in 1922 arrived at the conclusion that the glycuresis represents not utilizable sugar, but carbohydrate moieties from food rendered unassimilable by processes of cooking and baking. Laug and collaborators (7, 8), in reports of studies on the nature of the reducing substances in the urine of dogs fed diets containing bread crusts, found evidence of the presence in the urine of non-reducing, non-fermentable substances which on mild acid hydrolysis yielded reducing, non-fermentable substances. These in turn gave reducing fermentable end products on further hydrolysis. They supplied evidence of an indirect nature indicating the materials whose hydrolysis yields extra fermentable reducing substances are not of nitrogenous origin. However, the authors did observe that increases in non-fermentable reducing substances were accompanied by well-marked rises in total nitrogen excretion. More recently Friedman and colleagues (9), in an investigation of the nitroprusside - and hydrazine-reactive substances in the urine of humans after the ingestion of heat-processed foods (Army ration items), reported evidence of the presence of neutral carbonyl compounds and keto-acids. The quantities of the carbonyl compounds present correlated with the ingestion of "browned" foods. Since the carbonyls which appear in urine, although derived from food, cannot be identified with any known decomposition products of carbohydrate or protein it appears that the intervention of metabolic processes is required for their formation from heat altered foods.

A number of studies of the deleterious effects of heat on the nutritive value of the proteins of cereals have been reported more recently. At least a part of this loss in nutritive value may be attributable to browning. Peters (10) carried out studies on oat proteins subjected to heat treatments and concluded that the degree of heat treatment determines the manner in which the nutritive values are reduced. Relatively mild processing, such as steam cooking of oat dough, does not cause appreciable loss of lysine when assayed after acid hydrolysis. The amount of lysine released by in vitro enzymic digestion is appreciably less. Toasted oat flakes exhibited a slight destruction of lysine, recoverable by acid hydrolysis, and an even more pronounced reduction in that releasable by enzymic action. The more severe treatment undergone in the gun explosion process is accompanied not only by retarded releases, but also by a significant destruction of lysine. In the more extreme treatment the decrease in the rate of enzymic release of lysine is great enough so that the length of time that the proteins are subjected to the action of the animal's proteolytic and absorptive mechanisms resulted in a three-fold lysine fecal excretion. This retarded digestion may be of great nutritional importance in view of the evidence now available indicating a significant time relationship in absorption of the essential amino acids and the essentiality of simultaneous availability of acids if deficiencies are to be avoided. The lysine that may be lost through the formation of products which tie up the amino acid through combinations with carbonyl groups, and which are non-hydrolyzable, was not estimated.

An additional reason for the Armed Forces' interest in the browning reaction is that of the possibility that the intermediate, or end products, of the reaction may prove to be toxic in the amounts consumed under the conditions of feeding experienced in military services.

Raisins, dried figs, and prunes represent products in which the establishment of food habits has, through time, resulted in acceptance of the items. They are not, according to the experience of populations, considered toxic. However, it is not the usual practice to subsist on diets which contain considerable quantities of these dried fruits over periods of weeks or months. These dried fruits are laxative, and this may indicate toxicity of some of the intermediates or final products of the reactions. There appear to be three possibilities of toxic action: first, toxicity in the usual sense of tissue injury; second, the result of removal from the absorbed foods of some component required in the metabolism of growth and maintenance of the best physiological state, i.e., creation of deficiencies; and third, the possibility of intermediates of carbohydrate fragmentation replacing some essential nutrilite in a series of metabolic reactions. The latter is the antimetabolite concept. Probably the more likely of the possible replaceable metabolites is ascorbic acid, since carbohydrate fragmentation may take place through the formation of intermediates possessing some of the chemical properties of the vitamin (11).

That trace metals, acting as catalysts, may play a significant role in browning is indicated by the work of Thompson, et al (42). These workers have shown that copper may combine with proteins and that the resulting copper protein complexes will react with compounds containing an ethylene bond - for example, ascorbic acid - to form ring structures which possess browning characteristics.

Browning in Fruits and Vegetables

Discoloration in fruits has probably received more attention than that of any other product group. Non-enzymic browning appears to occur in almost all dried fruit products and in fruit juices and juice concentrates. The significance of browning in relation to quality, however, may vary markedly with the product. Custom and food habits have made dried prunes and raisins, for example, acceptable while what are probably similar changes in dried apricots or citrus juices may result in complete consumer rejection. Most of the research of the past has been directed at efforts to find preventatives without first having found the causes. Stadtman, in his recent review of "Non-Enzymic Browning in Fruit Products" (12), draws attention to the various theories of browning; namely, the Maillard or melanoid condensation, ascorbic acid, and the "active-aldehyde" theories. The Maillard reaction involves a condensation of amino acids and reducing sugars and gives rise to the formation of dark-colored substances. According to the ascorbic acid theory, the colored products are formed by the oxidation of ascorbic acid and related compounds. The "active-aldehyde" theory postulates the decomposition of sugars and sugar acids to furfuraldehydes or similar compounds characterized by having an active carbonyl group, and that these products condense with nitrogen compounds. The role of the nitrogen compounds is not yet clear, however, and there is increasing evidence that they exert a catalytic effect on sugar decomposition and form condensation products as well. Stadtman points out that actually all three of the postulated mechanisms may be involved in the browning of fruits. In each of the three postulated series of reactions the oxidation and/or condensation products are held to polymerize to form pigments. These dark pigments produced in various fruit preparations are indistinguishable by the method thus far employed for their study. Efforts to follow quantitatively the changes in ascorbic acid, reducing sugars, and amino acid contents of browned fruits have not yielded completely satisfactory evidence leading to clarification of the problem, since the results are not in agreement for a given fruit product and may be at marked variance when different fruits are observed. It seems clear that browning in citrus fruit juice is always associated with destruction of ascorbic acid. It appears that the color may develop without marked change in the amino acid content. On the other hand, analysis of the dried fruit for amino nitrogen, and studies carried on by ion exchange removal of the cationic nitrogen complexes, supply strong evidence that amino acids do play a part in dried apricot browning. The California group supplies evidence that three general types of reactions resulting in browning take place in dried apricot extracts: (1) reactions involving nitrogen compounds and sugars, (2) reactions involving organic acids and sugars, and (3) reactions involving nitrogenous compounds and organic acids. They emphasize that in these types of reactions several naturally occurring and derived compounds may undoubtedly participate. Galacturonic acid is especially active. They have observed that continuous extraction of apricot juice concentrates with ethyl acetate almost completely prevents the color changes and that several aldehydes, among them the furfuraldehyde, have been shown to be present in the extracts.

Of the vegetable products, dried potatoes have received the most concentrated attention. Much of the effort has been given to studies of varieties, with the view of selecting those which, when dried, will have the longest storage life; to investigations of the relation of maturity at harvest to browning; to a search for methods which, when applied to stored potatoes, will best enable selection of lots; and to a determination of what storage conditions will best insure the stability of the dried products. Reports by Bergdoll (13) show that the rate of browning of dried potato preparations are correlated with the amounts of reducing sugars present in the raw materials, provided the sugars amount to one percent or more on a dry weight basis. In samples with lower sugar values the correlation does not appear to hold. The tendency to brown was found to be usually, but not always, associated with high amino acid content. The Purdue group interprets its results as indicating the pigments to be derived by condensation reactions between carbohydrate materials and amino acids, though the isolated products are distinctly different from the synthetic glucose-glycine pigment. The California group (14) was unable to identify furfural derivatives by absorption spectra methods among the carbonyls extracted by ethylacetate from dried potatoes. Pyke (15) has investigated the relationship between reducing sugar content, storage time, and temperatures of potatoes immediately preceding drying and the browning rate in the dried product. He finds that by increasing metabolism rates, by holding in warm rooms for short periods and thus using up the accumulated sugars, it is possible to stabilize the dry products. Tempering at 72° F. for relatively short periods was found to be quite effective with selected varieties. An alternate procedure which it is hoped will widen the choice of varieties is being considered at the Institute. Milder heat treatment, which will minimize the conversion of starch to reducing sugars, seems encouraging even though much active peroxidase remains in the dry products.

Browning in Dairy Products

The development of a brown color has long been recognized by the dairy industry as an undesirable defect in many of its products. The color develops in sterilized evaporated milk, as well as in dried milk products and sweetened condensed milk, especially after storage. The browning is accompanied by insolubility and flavor defects. High moisture products have been observed to decrease in biological value, which appears to be correlated with a lowered availability of amino acids, especially lysine.

Investigations regarding the causes of browning in processed milk were reported as early as 1893 when Richmond and Boseley (16) found the color changes to be closely associated with decreases in lactose. In 1905, Orla-Jensen and Plattner (17) reached the conclusion that the changes are the result of reactions between casein and lactose. Each of the two theories, caramelization and protein-sugar reactions, appears to have support in the present day industry. In 1924, Wright (18) suggested a catalytic action by casein on the caramelization of lactose. McGreary (19), by accelerated storage studies on dried milk, observed a decrease in lactose content and also a decrease in amino groups as measured by formol titration. He suggested an aldehyde-amine linkage. Further evidence of such linkages and their significance in browning was supplied by Ramsey, Tracy, and Rueke in 1933 (20), by Stewart in 1942 (21), and also by Doob, Willman, and Sharp in 1942 (22). Stewart investigated some of the properties of the brown substances formed by heating mixtures of casein and lactose, or by heating dried milk. It was found that a ratio of approximately one part lactose to 20 parts casein by weight was required to produce a completely acid or alkali insoluble product, and that an excess of lactose showed no appreciable additional insolubilization, while a lactose concentration of less than the ratio 1:20 allowed the formation of only a partially insoluble product. Doob, et al examined browning in dried milk and whey. Dried wheys were found to brown more than dried milks on storage. The browning was explained as a reaction between lactose and protein resulting in an increased titratable acidity and a decrease in pH. The agreement regarding the interpretation of results of studies conducted by use of dried products does not appear to hold for the results obtained by examination of browned heated milk. Kass and Palmer (23) have stated that caramelization of lactose satisfactorily accounts for the brown color in heated milk. They observed slight increases in formol titration, but the Van Slyke amino nitrogen method showed no decrease in amino groups. By measuring lactose concentration polarimetrically they obtained data which showed a constant loss of the sugar when heated with varying amounts of casein. They believed their data to be sufficient to disprove any stoichiometric bifunctional reaction between aldose and amino groups to form definite lactose-protein compounds in heated liquid milk.

At present, no available powder meets the Armed Forces' requirements for beverage milk for inclusion in operational rations, since mechanical equipment for refrigeration and for dispersion are not available under the conditions where the powders are used. The more recent researches are designed to explore the nature of the changes in proteins, carbohydrates, and lipids that account for lowered dispersibility and the development of off-flavors, variously described as stale, caramelized, chalky, astringent, or gluey. This flavor is held to be distinct from the tallowy flavor resulting from changes in the lipid components.

Josephson and Patton (24) extracted sterilized skimmed milk with redistilled ethyl ether, removed the ether by distillation, and fractionated the resulting concentrated residue into three fractions; namely, petroleum ether soluble, water soluble, and ethyl ether soluble. The ethyl ether soluble fraction was further fractionated by distillation. One distillate collected between 57°- 59° C. gave reactions characteristic of the furan ring. It contained 60.15 percent carbon and 6.07 percent hydrogen. It did not contain nitrogen, sulfur, or halogen. The authors express the opinion that the distillate probably contributes little, if anything, to the caramelized flavor. A yellow oil isolated from the distillation residue, by petroleum ether extraction, was found to possess a pronounced odor of the caramelized variety. Elemental analysis demonstrated the oil to be high in sulfur, but negative for nitrogen and halogens.

Chapman and Moster (25) have modified the acid ferricyanide method for the determination of reducing substances and applied the modified method to browned milk powders and model systems composed of mixtures of proteins, amino acids, and lactose. In all heated preparations a qualitative correlation between browning and the development of reducing substances was observed. Since a loss of amino nitrogen was shown by the Van Slyke method, while the formol titration failed to indicate similar losses, these workers have assumed that a reaction involving an amino group, possibly lysine, takes place with the formation of an imino group which dissociates at a lower pH. An investigation of the titration curves obtained by use of heated and unheated powders showed an increase in the number of groups dissociating between pH 6 and 9.25, and a corresponding decrease in groups dissociating between pH 9.23 and 11.94. The same workers have found the production of reducing substances to be independent of processing temperatures, and of the type of atmosphere in the pack. A relationship has been found between the development of reducing substances and increases in the temperature and time of storage, but no direct correlation was observed between the reducing substances and the moisture content.

Coulter and Jenness (26) have also investigated the effect of time and temperature of heat treatment on the reducing substances in fluid whole milk and dry whole milk. Two methods were used to determine reducing capacity: (1) a modification of the acid ferricyanide method of Chapman and McFarlane, and (2) the thiamine disulfide method of Harland and Ashworth. The latter measures only the reducing groups produced as a result of heat treatment of the serum protein fraction. The acid ferricyanide method includes these groups as well as ascorbic acid and reducing materials resulting from heat treatment of lactose in the presence of phosphate buffer or protein. Reducing groups derived from the serum proteins reach a maximum and then decrease, as a result of oxidation, unless the milk is deaerated. The acid ferricyanide reducing groups, although showing some effect of oxidation, continues to increase over long periods of heating, and the increase proceeds at a maximum rate in systems of about 90 percent solids. Their production appears to be associated with the production of carbon dioxide, loss of lactose, loss of solubility, increased acidity, development of fluorescence, and browning. The fluorescing materials are apparently derived mainly from interactions of proteins and carbohydrates, although some seem to be of lipid origin.

Browning in Dried Eggs

Discoloration and the loss of functional properties of dried egg white are in all probability browning phenomena. It has been shown by various investigators that sugars are involved in the darkening of dry egg white and egg white powders. Removal of the sugar by fermentation of liquid egg white results in products which are color stable for many weeks at 40° C. storage. Furthermore, Stewart and Kline (27) and also Stewart, Best, and Lowe (28) have shown that the addition of as little as 0.1 percent dextrose to the sugar-free egg white before drying causes loss of solubility and development of pigment during storage for 12 weeks at 40° C. The replacement of glucose with sorbitol or methyl glucoside resulted in retention of solubility in experiments carried out by Bate-Smith and Hawthorne (29). Using yeast to remove sugar from whole egg pulp, Hawthorne and Brooks (30) demonstrated an improvement in the storage life of the dried products. Storage improvement was shown by the lowered rate of denaturation and browning, retardation of pH changes, and rates of development of fluorescence, creaming, and beating power.

Bate-Smith and Hawthorne (31) and Olcott and Dutton (32) found that proteins and amino acids play a role in browning of dried egg products as indicated by the results of determinations of the amino nitrogen as browning develops. Bate-Smith and Hawthorne found that additions of 5 to 10 percent glycine or alanine to unfermented whole egg pulps before drying resulted in retention of solubility, but that browning and fluorescence were not favorably affected. Of the several amino acids used, cysteine gave better results with respect to color. Kline and Fox (33) have reported similar favorable experiences with cysteine and attribute the inhibition of color development to the formation of a cysteine-glucose compound which is relatively stable and colorless.

There is a marked lack of correlation between development of salt soluble fluorescence and palatability in whole egg powders dried to moisture contents of 2 percent and below. Fluorescence measurements, as estimates of browning, are usually conducted by using aqueous extracts. However, lipid solvent extracts of browned whole egg powders remove much of the color. There is evidence that protein insolubilization by browning reactions may account for solubility and texture changes and also functional property losses, while lipid browning accounts largely for the flavor changes. Investigations of the lipid soluble brown pigments by Edwards and Dutton (34, 35) disclosed evidence that they are derived from reactions between cephalin and carbonyl groups. This evidence is based on the similarity of light absorption properties of the brown pigment concentrates obtained from deteriorated powders, and those of synthetic pigments prepared by reacting ethanolamine (the amino moiety of cephalin) with acetaldehyde. Kester (36) found the amino nitrogen of cephalin preparations from slightly deteriorated powders is lower than that from fresh powders, but it is restorable to a considerable degree by acid hydrolysis. However, the cephalin amino nitrogen from extensively deteriorated powders was found to be only slightly restorable by acid hydrolysis.

Browning in Meat and Cereal Products

There appears to have been little effort to investigate the significance of browning as a deteriorative factor in meat products. Since the glycogen present in muscular tissues is broken down to lactic acid by enzymic action during rigor and aging without the accumulation of aldehydes, it does not seem that the carbohydrates are a likely source of carbonyl groups. The possibility of intermediates of fat oxidation supplying carbonyls has not – to the knowledge of the writer – been investigated.

Mixed meat and cereal products, such as those supplied as soup mixes are a likely medium for browning. Especially is this true where protein hydrolysates are added as flavoring agents. It is interesting to note in this connection that Maizel (37) reports that time, temperature, and pH are significant factors in developing desirable flavors in such mixes using yeast autolysates. Flavor development is reported to pass through an optimum and then subsequently to decline. Anson (38) has directed attention to the possible significance of browning where monosodium glutamate is used as a flavoring agent in preparations containing reducing sugars. Of significance to the meat packing industry is the observation of Elvehjem (39) that in the case of some of the Army's packaged rations supplementation with casein produces a marked improvement in the growth responses of the test animals. It does not follow that supplementation of the products with casein prior to processing will correct the differences since casein undoubtedly is subject to the same reactions as the included meat proteins. The work of Beuk, Chormock, and Rice (40) is of possible interest in this connection. They have recently reported the results of a study of the effect of severe heat treatment (112° C. for 24 hours) upon the amino acids of fresh and cured pork. Analyses of acid - or alkali-hydrolyzed autoclaved samples - indicated complete retention of arginine, histidine, isoleucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. The retention of cystine was 56 percent. Hydrolysis with trypsin followed by erepsin resulted in apparent low retention (27 to 65 percent). However, treatment of the enzyme hydrolysates with acid permitted recovery of the initial amounts of all the amino acids except cystine. Part of the bound amino acid fraction is soluble but unavailable to both bacteria and rats. They suggest the possibility that the milder processes of home or commercial cooking likewise decrease digestibility, but that the changes may not be detectable under normal conditions.

To return to cereal products, recent reports by Geddes and associates (41) supply additional information on the character of the brown pigments which are formed in canned breads stored in metal cans at temperatures ranging from -15° C. to 75° C. Reflectance measurements show browning to occur in bread samples stored at temperatures simulating those of the tropics. Analyses of browned and unbrowned bread crumb for total soluble nitrogen, titratable acidity, amino nitrogen, available lysine nitrogen, and reducing sugars often gave differences which were very slight, whereas in the same samples the brown color was markedly different. Even in those cases where the results of analysis were markedly different, there was a question regarding proper interpretation, since most of the methods were highly empirical. Marked browning is accompanied by a "disappearance in available lysine." Water and a number of organic solvents, including ethyl acetate, were used in an endeavor to extract the pigments from the crumb. Only slight extractions were achieved. However, extraction with water following acetylation of the crumb by use of acetic anhydride in dry pyridine removed the pigments. The acid hydrolysates of the aqueous extracts from bread stored at 75° C. for 17 days and from unstored bread showed some differences in amino-nitrogen as measured by the Van Slyke method. Ligh absorption of aqueous extract concentrates occurred in the wave length range of 225 mu with a peak at 255 mu.

Inhibition and Control of Browning

There appear to be a number of precautions, generally applicable, that may be taken to minimize unfavorable browning during processing and storage of food items. Perhaps the cardinal one is the avoidance of processing procedures which result in carbohydrate and protein hydrolysis. The use of excessively high temperatures applied for unnecessarily long periods is obviously undesirable. The temperature coefficients of the aldehyde-amine reactions are large, and low temperature storage, where feasible, can be expected to be useful in extending storage life. Increasing the carbonyl and free amino acid contents of the products, either by additions or through unfavorable storage conditions of the raw materials, leads to adverse results. Reducing the concentrations of the same reactive groups may be feasible in some instances. Fermentative removal of glucose from egg white is an old practice. Perhaps the removal of amino compounds by use of ion exchange materials will also find application in the stabilization of some products.

Control of the moisture content may also be helpful. Any reaction in solution in which two or more components take part is highly sensitive to the concentration of the reacting components. Thus, in dilute systems browning may be expected to proceed at low rates. As the systems are concentrated the rate increases rapidly until the moisture content is such that a maximum reaction rate is reached. Stadtman (12) points out that apricots dried to 0.4 - 0.7 percent moisture may be held in good condition for three years. Under anaerobic conditions the maximum rate of darkening was found to occur at 5 - 10 percent moisture. Increasing the moisture content from 10 - 25 percent was accompanied by 15 - 30 percent increase in storage life. The beneficial effect of higher moisture was lost when the oxygen content in the pack was increased to 200 mgs. O_2/100 grams of fruit. Concentration of orange juice to 65° Brix shortens the storage life markedly. At 80° F. storage, e.g., the product may darken, gas form, and marked flavor deterioration may result. Neither pasteurization nor sodium benzoate treatment influenced the course of the deterioration (43). Single strength juices are more stable under similar storage conditions (44). In powdered whole eggs the type of browning reaction appears to change as the moisture content is lowered. The rate of the dominant reaction, which results in insolubilization and changes in texture, is markedly decreased by reducing the moisture to 2 percent or lower. However, browning in which lipids play a part is not retarded at the same rate and appears to become dominant at the lower moisture contents.

In general, exclusion from oxygen is beneficial, though the degree of improvement varies markedly with the several commodities. In products which contain ascorbic acid and high moisture content, as the citrus juices, oxygen exclusion prolongs the storage life. In dried fruits the rate of darkening is proportional to the rate of oxygen taken up by the fruit which is in turn related to the moisture content of the samples(11). Coulter (45) concludes that oxygen is not a factor in browning of milk powders though its exclusion aids in retarding undesirable changes in the fats. Packaging in inert gases notably extends the storage life of low moisture (2 percent) whole egg powders. Here the deterioration appears to be primarily attributable to a cephalin-carbonyl reaction. Kester (36) has pointed out the possibility of fatty acid peroxide rearrangements to form alkenols and epoxides which may be expected to react with amino groups in the same molecule.

Control of pH may be useful in some types of products. Melnick (46) proposes to lower the pH of soup mixes and add sufficient alkali to the dry products to restore the reconstituted materials to a near neutral pH. Boggs and Fevold (47) have found the storage life of whole dried egg powders, as estimated by retention of palatability and aeration properties, to be notably prolonged by lowering the pH of the egg pulp to 5.5. Solid sodium bicarbonate is added to the powders in sufficient quantity to neutralize the added acid upon reconstitution. Smith (48) has correlated the pH of potato juice before and after processing with the presence or absence of discoloration of the finished products. He has also explored the usefulness of acidification of the tubers and reports marked extension of storage life.

Sulfur dioxide has been used to prevent discoloration of some dried fruits for many years. There are at least three theories of sulfur dioxide inhibitory action: (1) antioxidant action, (2) addition to carbonyl groups, and (3) bleaching. Neither theory offers a completely satisfactory explanation. A better understanding of the mechanisms of this inhibitory action would, no doubt, be very helpful in elucidating the chemistry of browning. A number of other treatments of fruit products have been suggested, including use of sugar sirup before drying. The use of various chemicals has been investigated. Those most effective, such as formaldehyde, may serve as tools in the study of the reactions, but are of little practical use.

Browning of food commodities is not necessarily undesirable. There are instances in which the reactions are a requirement in the attainment of characteristics demanded by consumers. A few such products are maple sirup, baked cereal products, protein hydrolysates, roasted nuts, beer, cured tobacco, and coffee brew. Most of these flavors are the results of empirically controlled processing conditions. In some, as soluble coffee preparations, the extent of the reaction can readily get out of hand.

As experience in procurement, transportation, and storage of food items accumulated during World War II, it became obvious that many of the difficulties in maintaining adequate nutrition and prevention of wastage because of lowered acceptance could be traced to quality deterioration through browning. Late in the war the Quartermaster Food and Container Institute undertook the sponsorship of researches on browning problems. While these researches have not yielded solutions, they have stimulated effort that can be expected to result in a much better understanding of the problems. Concerted rational attacks upon deteriorations of a wide variety of products have resulted. At all events, a rational basis for applied research is being established.

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