Chemical Changes in Dehydrated Milk During Storage

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Chemical changes in dehydrated milk cause staleness, oxidized flavor, hydrolytic rancidity, and insolubility to an extent influenced by the processing treatment, moisture content, free oxygen level within the container, and storage temperature. The exact causes and chemical reactions involved in staling are complex and partly obscure. High moisture promotes staling. Certain stale flavors are associated with protein fractions of milk involving denaturation and partial hydrolysis; others have been attributed to incipient oxidation of the lipide fraction. Oxidation of milk fat by atmospheric oxygen results in tallowy flavor. The rate of fat oxidation can be reduced by the addition of antioxidants. High heat treatment of fluid milk before drying will moderately decrease rate of oxidation by producing reducing compounds, but will impart a cooked flavor to the final product. To date the most effective method of preventing oxidative deterioration is lowering the free oxygen level in the container to, or below, 0.01 ml. per gram of powder. Hydrolytic rancidity is not common in dehydrated milk, because the milk lipase is inactivated by heat treatment. Browning reaction leading to caramelized flavor and pronounced loss of solubility will occur if the moisture content of dehydrated milk is increased to 4% or over and the storage temperature is high.

THE KEEPING QUALITY OF DEHYDRATED MILK during storage in the warehouse, in the retail store, or on the kitchen shelf is of great importance to consumer acceptance. To maintain the high quality of the product in storage, it is necessary to prevent chemical reactions causing the formation of various compounds that impart a more or less undesirable flavor to the reconstituted milk. Research in this field was considerably stimulated by the purchase of large quantities of dehydrated milk by the armed forces during World War II. The knowledge thus gained regarding keeping quality made it possible for the dry milk industry to expand both its domestic and its export market by improving methods of processing and packaging to give a maximum protection against chemical deterioration during storage.

The chemical reactions involved in the deterioration of dehydrated milk during storage can be grouped in the following types:

Maillard reaction between milk proteins and lactose. This reaction, in presence of high moisture content (4% or more), leads to the rapid browning of the product with development of caramelized flavor and loss of solubility.

Oxidation of nonlipide fractions by atmospheric oxygen, causing development of from "stale" to "burnt feather" flavors depending on the moisture content and temperature of storage.

Oxidation of the lipide fraction by atmospheric oxygen with production of aldehydes, ketones, and other compounds.

Hydrolytic splitting of milk fat caused by insufficient heat treatment of the milk before drying and thereby insufficient inactivation of lipolytic enzymes, with resulting development of a rancid flavor by formation of free fatty acids.

The rate of these chemical reactions will depend on one or more of the following factors, which are controllable by the manufacturer:

Heat treatment of the milk before drying.
Deaeration of the milk before heat treatment.
Copper contamination from process equipment.
Homogenization.
Method of drying.
Original moisture content of the powder.
Absorption of moisture during storage.
Level of atmospheric oxygen in the package.
Temperature of storage.

Low moisture content of the dry product, low level of oxygen in the package, and moderate temperature of storage are the most critical factors in controlling the keeping quality. The type of predominant off-flavors developed during storage by the chemical reaction mentioned above depends largely on the fat content. Only whole milk powder develops a tallowy flavor by oxidation and the "stale" flavor developed with high moisture in whole milk powder exposed to air is modified by the presence of fat. The off-flavor also depends on a combination of the factors influencing the rate of each reaction. In many cases the off-flavor of the product is caused by several chemical reactions resulting in a combination of various types of flavor.

Stale Flavors

The initial off-flavor developed during the storage of whole milk powder which has been well gas-processed to a low oxygen level to protect against fat oxidation is difficult to classify and for lack of a better description is often referred to as a slight stale flavor. Whitney and Tracy (*28*, *29*) found that the stale flavor in gas-packed whole milk powder appears to be distributed between the fractions of cream, washed cream, butter, and butter oil according to their milk fat content and therefore is concentrated in the fat phase. These authors admit, however, that their tests do not prove the origin of the stale flavor. Henry *et al.* (*7*) studied the keeping quality of dehydrated skim milk gas packed and air packed, with varying moisture content and at different temperatures of storage. They suggest that a stale flavor with gluelike character is developed as a combination of an initial Maillard reaction and oxidation; but they also found that dehydrated skim milk with a low moisture content, which minimizes the Maillard reaction, would develop in presence of air an off-flavor with less "gluelike" character, possibly caused by oxidation of the small amount of fat present although a tallowy flavor could not be specifically identified. Coulter *et al.* (*2*) state that considerable changes in palatability often occur before any significant changes in the chemically detectable manifestations have taken place. Such deterioration of flavor, they state further, can be retarded by reducing the moisture content to a low level and by packing in inert gas in hermetically sealed containers; but even the best commercial practices currently available do not entirely prevent the development of staleness. Storage at a reasonably low temperature of 15° C. (59° F.) or below would tend to reduce the development of the stale flavor in dehydrated milk of low moisture content and low oxygen level.

Maillard and Browning Reaction Flavors

The browning of dehydrated milk in storage is a function of its moisture content and temperature of storage (*1*, *3*, *7*, *24*). The browning does not take place when dry milk is stored at 40° C. (104° F.) or lower if the moisture content is below 4% (*24*). The browning of high-moisture milk powder is preceded by the Maillard reaction between amino groups and lactose (*7*). The brown color is developed by degradation of the amino-aldehyde compounds and caramelization of lactose. The moisture content of commercial dry milk is usually below 3%. Dry milk stored in containers that are not moistureproof will invariably absorb moisture from the surrounding atmosphere, developing brown discoloration. The changes accompanying the brown discoloration of milk are: uptake of oxygen, production of carbon dioxide, increase in acid ferricyanide reducing substances, decrease in solubility, and development of caramelized flavor (*24*). Tarassuk and Jack (*24*) observed that in powders of moisture content above 4% stale and burnt flavors preceded the development of caramelized flavor, but low oxygen level favored the development of typical caramelized flavor only. These authors concluded that staleness of dry milk with normal or low moisture (moisture below 3%) is not related to reactions responsible for browning, as in these powders staleness develops in the absence of brown discoloration. However, Henry *et al.* (*7*) found that the Maillard reaction, the reaction between the free ϵ-amino groups of proteins and the aldehyde groups of reducing sugars, takes place in milk powder at all levels of moisture but at various rates, and the initial protein-sugar complex is not colored brown. The Maillard reaction, therefore, might also be one of the contributing causes for stale flavor development in milk powder of normal or low moisture content. Lea (*13*) found that glucose reacted with milk proteins much faster than lactose.

Henry *et al.* (*7*) showed that the progress of the formation of the protein-sugar complex can be followed directly with the Van Slyke method for free amino nitrogen, and that lactose is bound by this reaction so that it becomes undialyzable in the proportion of one molecule of lactose for each free amino group destroyed. These investigators also showed that the protein-sugar complex reaction comes to a stop when 30% of the free amino groups as determined by the Van Slyke method still remains undestroyed. They conclude that this is probably due to the heterogeneity of the solid protein-sugar mass, but it could also be explained by assuming that part of the lysine amino groups may be less favorably placed for reaction with sugar molecules. They made an interesting observation that there is a relatively rapid drop of 3 to 6 units in free amino nitrogen content with medium and low moisture skim milk powder, which occurred early in the storage at 37° C. (100° F.), followed by a much slower linear change. They suggest that this might be caused by the presence of a small amount of reactive material, which could be either (*a*) a small proportion of protein amino groups of greater than average activity or accessibility or (*b*) a small proportion of a reducing sugar more reactive than lactose, such as glucose, which has been reported by Whitnah (*27*) to be present in milk. The British investigators, however, think that the more likely explanation for this rapid initial reaction is the variable accessibility of the reacting groups to one another in the solid system. Henry *et al.* (*7*) calculated that for dehydrated skim milk with 7.6% moisture the rate of formation (and degradation) of the protein-sugar complex increased by a factor of about 6 for each 10° C. increase in temperature, but at a lower moisture of 3.0 to 5.0% the temperature coefficients were of the order of $Q_{10} = 2$.

Coulter *et al.* (*1*) also studied the effect of moisture on the keeping quality of whole milk powder at various temperatures. They found that an increase in the moisture level causes development of stale to a "burnt feathers" flavor, production of acid ferricyanide reducing substances, production of carbon dioxide, and utilization of oxygen. They showed that during the initial stages the rate of change of each of these reactions increases logarithmically with the increase in moisture content. They state further that in adequately gas-packed dry whole milk a minimal moisture content appears desirable, and that the rates of change in every instance are very slow in powders containing 2% or less moisture.

Tallowy Flavor

The most serious defect of whole milk powder in storage is caused by oxidation of the fat by atmospheric oxygen, with production of aldehydes (*17*). Heptyl aldehyde, octyl aldehyde, and nonyl aldehyde have an odor resembling old tallow. Schibsted (Shipstead) (*18*) showed in the disclosure of his patent of 1932 that tallowy flavor of spray-dried whole milk powder in storage could be prevented completely by reducing the atmospheric oxygen content of an air-tight package below 5 ml. per pound of powder. This was done by double evacuation with an intermediate holding time of about 18 hours, which allowed part of the occluded oxygen inside the spray powder particles to diffuse out into the free space between the particles, from which it was removed by the second evacuation. Lea *et al.* (*14*) during World War II confirmed the findings of Schibsted (Shipstead) (*18*) by stating that the best keeping quality of spray-dried whole milk powder could be obtained by reducing the oxygen level to 0.01 ml. per gram of powder (4.5 ml. per pound). They also demonstrated that a given degree of tallowiness is not always produced by equal uptakes of oxygen. Powders in which tallowiness is produced slowly require more oxygen for a given degree of tallowiness than those which deteriorate rapidly, because oxygen is also used up by the solids-not-fat fraction. The longer the induction period of fat oxidation, the more oxygen relatively is used up by the solids-not-fat fraction.

The keeping quality of whole milk powder stored in presence of air can be improved by eliminating completely any contamination by copper during the processing of the liquid milk before drying. This has long been known in the dry milk industry, and when stainless steel became available all copper or copper alloy equipment was replaced. In the Quartermaster's specifications for whole milk powder, the maximum limit for copper content was set at 1.5 p.p.m. Hollender and Tracy (*8*) have shown that addition of 3.7 p.p.m. of copper (powder basis) after preheating had a marked effect on the rate of development of tallowy flavor, and that addition of antioxidants did not entirely overcome the effect of copper contamination.

Holm *et al.* (*9*), Mattick *et al.* (*15*), and Jack and Henderson (*10*) studied the effect of high preheat treatment of the fluid milk before drying, and found that it improves the keeping quality of whole milk powder in presence of air. According to Holm *et al.* (*9*) there seems to be an optimum temperature of 83° C.

(181° F.) for preheating of whole milk for 30 minutes, which they attribute to greater enzyme inactivation. Coulter *et al.* (1) suggest that of many reducing substances developed by preheat treatment those that are determined by the thiamine disulfide method (6) possess the highest antioxygenic effect. Greenbank and Wright (5) demonstrated that deaeration of the fluid milk before the preheat treatment in manufacture of whole milk powder resulted in an improvement in keeping quality of the powder in presence of air. This is explained as resulting from an inhibition of oxidation of the reducing compounds formed during preheating because of absence of dissolved oxygen in the fluid milk.

High preheat treatment in the manufacture of dehydrated whole milk improves to a limited extent the keeping quality in storage without gas-packing. The products, however, have a pronounced cooked flavor, which is objectionable to many consumers. In bulk sale to candy makers and bakers, whole milk powder is usually packed in barrels or drums without gas-processing. For this purpose the milk should be preheated to a fairly high temperature to improve its keeping quality. The same effect could be obtained by adding a suitable antioxidant to the fluid milk before drying, but permission for the use of such antioxidant must first be obtained from the Food and Drug Administration.

The moisture content of dehydrated whole milk is of importance in respect to both tallowy flavor and stale flavor. Coulter *et al.* (1) indicate that high moisture promotes the development of stale flavor and some moisture is necessary for the effectiveness of certain antioxidants. Therefore, low moisture content in whole milk powder would tend to accelerate the oxidation of the butterfat and development of tallowy flavor (19). The higher moisture content will cause the development of reducing substances associated with the initial Maillard reaction between amino groups and the lactose and these reducing groups will assert a retarding effect on the oxidation of fat.

The method of drying has certain effects on the rate of fat oxidation, caused by its action on the fat dispersion as well as the heat treatment in the drying operation. In the open-roll drying method, the butterfat emulsion is broken and the fat appears in relatively large masses on the flake particles with a small surface per unit fat exposed to the atmosphere, which tends to reduce the rate of oxidation. At the same time the heat treatment during the drying process develops reducing compounds that retard the fat oxidation. In the vacuum-roll drying process, the heat effect during drying is eliminated, but the fat dispersion is the same as in the open-roll powder. In the spray process it is considered desirable to have the butterfat well dispersed, so that it will not rise or deposit on the glass in the reconstituted milk. This is accomplished by the homogenizing effect of the high-pressure spray nozzle or by homogenizing the condensed milk when low-pressure spray nozzles or the centrifugal spray method is used. The fat in spray powders is therefore very well dispersed, and it appears under the microscope as minute globules evenly distributed in the solids-not-fat, partly exposed on the surface but mainly inside the spray-powder particles. The heat effect in the spray-drying operation is practically negligible if the powder is removed continuously from the drying chamber and cooled below 50° C. (122° F.) within a few minutes after removal. Powder left in the drying chamber for an appreciable length of time tends to become discolored and less soluble.

It was found by Shipstead (19), when extracting the fat with petroleum ether from a spray-dried whole milk powder, which had just turned tallowy, that the small amount (about 4%) of extractable fat on the surface of the spray-powder particles had become colorless and tallowy. However, when the remaining fat inside the particles was extracted with more petroleum ether after addition of 8% water, the fat had the normal yellow color and good flavor. This interior fat had apparently been protected from oxidation by the dense mass of solids-not-fat consisting mainly of a glasslike lactose with proteins and salts in a homogeneous mixture, whereas the surface fat with a relatively large surface exposure per unit fat was oxidized to a point of complete loss of color and development of a tallowy flavor. In a study of butterfat oxidation Schibsted (Shipstead) (17), using his test for "fat aldehyde value," found that with a fresh sample of butterfat it became colorless on absorption of 0.3 ml. of oxygen per gram, after which it began to develop aldehydes at a fast rate. During the induction period the carotene was being oxidized, and only after that did the butterfat develop a tallowy flavor. Since only about 4% of the total fat is exposed on the surface of the particles, it is evident that in 1 pound of whole milk powder with 26% fat, only about 4.7 grams of fat is involved in oxidation. This corresponds to only $4.7 \times 0.3 = 1.4$ ml. of oxygen for complete bleaching of the exposed fat per pound of powder. With further absorption of oxygen the exposed fat will take on an increasingly stronger tallowy flavor. Some of the available oxygen is undoubtedly used up in oxidation of solids-not-fat. The distribution of the atmospheric oxygen between the fat and solids-not-fat depends on a number of factors, as discussed above. These calculations indicate why only a relatively small amount of atmospheric oxygen can make spray-dried whole milk powder go off-flavor, and why it is so important to have a very low oxygen level in the package to ensure good keeping quality in storage.

Hydrolytic Rancidity

The occurrence of hydrolytic rancidity in dry milk is not so common as the occurrence of oxidative rancidity. During the war, the Quartermaster Corps Dairy Products Research Laboratory found occasional lots of dry milk possessing typical rancid flavor, resulting from partial hydrolysis of fat. This flavor is characterized by a bitter taste and sharp unpleasant odor resembling butyric acid, and it is due to lipolysis and the resulting appearance in the product of free fatty acids (from butyric through myristic).

Although the literature on lipolysis in liquid milk is extensive, the information available on lipolytic activity in dry milk is limited to a few observations. Nair (16) studied spray powder made from milk possessing some lipolytic activity. He failed to detect hydrolytic rancidity in reconstituted milks and concluded that lipolysis in milk powder is limited by a low moisture content and is not an important factor in contributing to objectionable flavors. Supplee (20) and Tarassuk and Jack (25) demonstrated conclusively that the lipolytic enzymes are capable of activity in moisture concentration as low as those found normally in milk powder. Hydrolytic rancidity in dry milk, therefore, can result either from lipolysis in the powder during its storage or when the powder is made from milk which had undergone lipolysis before drying.

Lipase System Of Normal Milk Two different lipase systems have been found to exist in cow's milk (21–23). One of these is present in all raw milk, but it becomes active only after certain treatments, such as homogenization (4), agitation of warm milk (12), warming the precooled milk to 30° C., and cooling again to below 10° C. (11). The activation is evidently due to the disruption, distortion, or partial replacement of the membrane material surrounding fat globules. In manufacture of dehydrated milk products the milk is subjected to lipase activation treatment at two stages of processing: homogenization and pressure spraying. However, the lipase activated by these treatments is easily inactivated by heat. As all milk is subjected to a preheating temperature equivalent at least to pasteurization prior to drying, the lipase of normal milk cannot be the cause of lipolysis in dry milk.

Naturally Lipolytically Active Milk This milk usually comes from cows that are late in lactation and are on dry feed—i.e., under the conditions that prevail in winter. This milk exhibits a spontaneous lipolysis, since the only condition necessary to initiate the hydrolysis of fat is the cooling of milk (*26*). Tarassuk and Jack (*25*), using exclusively this type of milk, prepared a series of spray-dried whole milk and ice cream mix powders, varying preheating temperatures from 71° C. (160° F.) to 93° C. (200° F.) for 12 to 15 seconds. The powder was packed ungassed and gassed and stored at 21° C. (70° F.) and 38° C. (100° F.). Their data show that relatively low moisture content of dehydrated milk is not a limiting factor of milk lipase activity. If a dehydrated product is made from naturally lipolytically active milk (requiring no other activation than cooling of milk), hydrolytic rancidity will develop in powder upon aging. The lipolytic activity in this case is not stopped by preheating the milk before drying as high as 93° C. (200° F.) for 15 seconds. How high it is necessary to heat milk before the lipase of naturally lipolytically active milk is completely inactivated has not been established.

It has been observed that the acid degree of fat in powder has to be about 4.0 or above before hydrolytic rancidity can be recognized organoleptically in reconstituted milk. In fluid milk hydrolytic rancidity can be organoleptically detected when acid degree of milk fat is about 1.0 or above. It is possible that an incipient hydrolytic rancidity of dry whole milk which is not recognized organoleptically may be criticized as stale.

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PECTIN GRADING

Application of Intrinsic Viscosity

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A study was undertaken to provide further information on tests for pectin grading, as a poll of American preservers has shown 71% in favor of a breaking measurement of the plunger type and 24% in favor of a rigidity measurement. A balance-plunger apparatus was developed, by which both small deformations and breaking strengths can be measured. Grades obtained from these measurements generally differ, but curves of intrinsic viscosity vs. grade can be used to estimate grade by elasticity, if grade by breaking has been determined, or the reverse if grade by elastic modulus has been determined. The curves and viscosity measurement alone offer a rapid and fairly reliable means of obtaining pectin grade values that would be procured by gel measurements of both types.

IN A POLL OF AMERICAN PRESERVERS (*10*), undertaken to determine the type of test preferred for pectin grading, 71% favored a breaking measurement of the plunger type while 24% preferred a rigidity measurement. The remainder (5%) considered both tests necessary. This paper reports a study undertaken to provide further information about the two properties involved and their relationship to intrinsic viscosity. A balance-plunger apparatus is described, with