PEARSON NEW INTERNATIONAL EDITION

Foods
Experimental Perspectives

Margaret McWilliams

Seventh Edition

ALWAYS LEARNING

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changes, with the color ranging from a pale golden brown to a gradually deepening brown before burning actually occurs. Similarly, the flavor begins to assume new and distinctive overtones as the mixture of sugar derivatives undergoes change.

The overall process of caramelization involves a number of steps, beginning with the inversion of sucrose (conversion to invert sugar). After the ring structures in the components of the invert sugar are broken, some condensation of the compounds occurs, which creates some polymers ranging in size from trisaccharides to oligosaccharides (as many as 10 subunits polymerized). Severe chemical changes at the very high temperatures involved also lead to dehydration reactions and the formation of organic acids and some cyclic compounds, as well as many other substances.

Caramelizing can be halted abruptly by adding boiling water to cool the extremely hot sugar mixture rapidly. Surprisingly, boiling water is much cooler than the caramelizing sugar. Of course, the addition of cool water also will halt the caramelization process. However, this practice is not recommended because of the extreme splattering and potential for burning one's skin that result when the two liquids come into contact and equalize their extreme differences in energy.

Evidence of the creation of acids during caramelization can be seen by stirring some baking soda into the caramelizing sugar, as is done in preparing peanut brittle. The carbon dioxide that forms when the soda neutralizes the acids creates a porous product as the gas expands in the hot, viscous candy solution.

The Maillard Reaction

An extremely important browning reaction in the preparation of foods is the **Maillard reaction**. This reaction, like the series involved in caramelization, is classified as **non-enzymatic browning**. Actually, the Maillard reaction is a series of reactions involving the condensation of a **reducing sugar** and an amine.

Maillard reaction
Non-enzymatic browning that occurs when a protein and a sugar are heated or stored together for sometime.

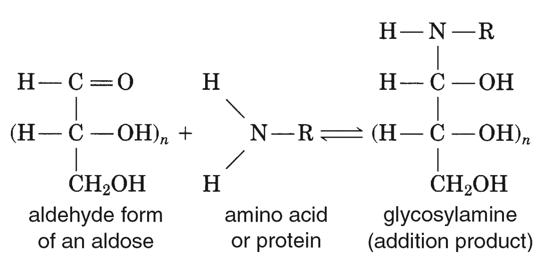
Non-enzymatic browning
Browning resulting from chemical changes that may be facilitated by heat.

Reducing sugar
Sugar having a free carbonyl that can combine with an amine, leading to non-enzymatic browning via the Maillard reaction.

Glucose, fructose, and galactose are reducing monosaccharides; similarly, lactose and maltose are reducing disaccharides. Lactose undergoes non-enzymatic browning most readily of the reducing sugars, followed in descending order by ribose, fructose, and glucose. These reducing sugars can combine with amines in milk and other protein-containing foods to cause non-enzymatic browning. Sucrose, however, is not a reducing sugar and does not participate in the Maillard reaction. It must undergo inversion to glucose and fructose before it can enter into this type of non-enzymatic browning.

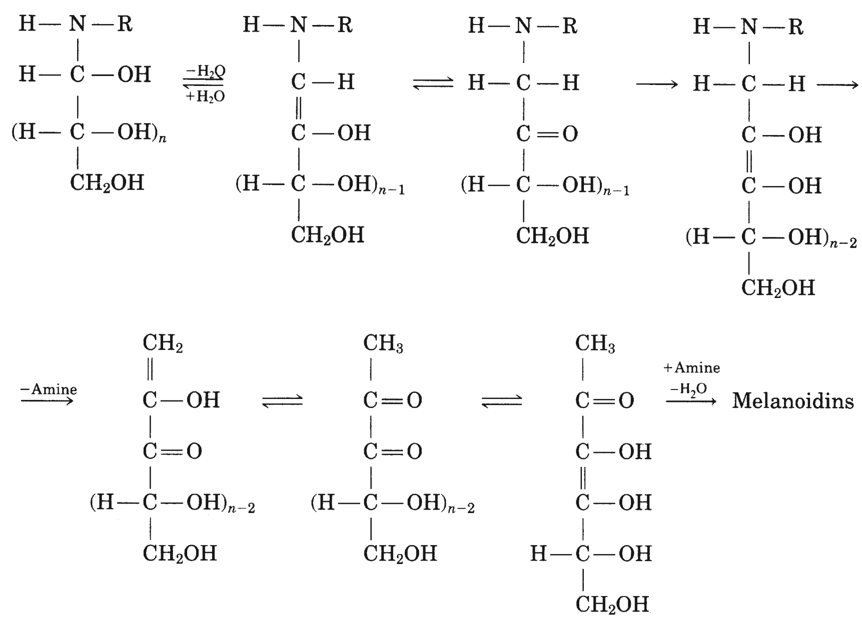
The color changes during the steps of the Maillard reaction occur rather slowly and with less energy input than is required for caramelization. The progression is from an essentially colorless substance to a golden color, on to a somewhat reddish brown and then a dark brown. This range of colors can be followed as caramels are boiled to their final temperature or during the baking of a plain or white cake as the crust color develops. Similarly, the reactions can be traced by watching the color development in sweetened condensed milk when it is heated in a water bath. A pH of 6 or higher accelerates the Maillard reaction.

The Maillard reaction proceeds rather quickly at elevated temperatures, but it also can occur at room temperature during extended periods of storage. In fact, one of the early problems in developing packaged cake mixes was prevention of the Maillard reaction, which sometimes occurred during prolonged marketing operations. The series of reactions appears to consist of many steps, with the first step probably being as follows:



Enolization Reversible reaction between an alkene and a ketone.

Through **enolization** and dehydration, colored pigments (melanoidins) are formed. The reactions outlined here are possible steps for this transformation.



Subsequent steps in the Maillard reaction

FUNCTIONAL PROPERTIES OF SUGARS

The sweet taste of sugar is utilized in many food products in amounts ranging from minute to the major ingredient, as in candies. When sugar-containing products are heated to very high temperatures, as occurs in candy making, the degradation products that begin to form contribute additional flavor components.

Sugars contribute color to products that are heated either to a high temperature or for an extended period of time (Figure 2). Part of the color noted on the surface of cakes is due to some chemical breakdown of the sugar, and part is the result of the Maillard reaction (nonenzymatic browning) that also is responsible for much of the color that develops while caramels are boiling. Caramelization is the key process responsible for coloring brittles and toffee, which are heated to a much higher temperature than are caramels.

Depending on their concentration in a product, sugars can have considerable impact on the texture of various food products. Sugar syrups become increasingly viscous as the sugar content is increased by boiling water away. Cakes become increasingly tender as sugar content is increased until a critical maximum is reached. Volume also is increased with some increase in sugar if the sugar level does not become so high that the structure ruptures, and the cake falls.

The effects of sugar content on the mouthfeel of candy are discussed in the next section. Sugar stabilizes egg white meringues and also causes the foam to have smaller cells and a finer texture as a result of the need for increased beating. In starch-thickened puddings, sugar serves as a tenderizing ingredient. Custards and other protein-containing products with increased sugar levels need to be heated to somewhat higher temperatures to coagulate the protein than is necessary when less sugar is used.

FOOD APPLICATIONS

Crystalline Candies

Crystalline candies Candies with organized crystalline areas and some liquid (mother liquor).

Candies that are easy to bite and have large areas of organized sugar crystals are categorized as **crystalline candies**. They are made by boiling sugar and water to concentrate the sugar syrup

Figure 2 The thick strand of caramel being inspected by this worker in Sri Lanka is a rich brown color due to the high temperature reached during boiling of the sugar solution.

sufficiently to form a firm, crystalline structure when cooled. However, most recipes contain other ingredients, too. For example, corn syrup or cream of tartar, butter or margarine, and flavorings such as chocolate or vanilla are included to enhance the quality of the finished product. Even with these additional ingredients, crystalline candies appear deceptively simple to prepare. In fact, they illustrate some key chemical and physical principles of food preparation.

Preparation. The quantity of sugar relative to the amount of liquid in crystalline candy recipes exceeds the amount that can be dissolved at room temperature. Consequently, the mixture feels gritty when stirred prior to heating. As the candy heats, the grittiness gradually disappears as more and more of the crystals dissolve. By the time the temperature of the boiling candy rises above 100°C (212°F), all of the sugar is in solution, and no crystals remain.

Water evaporates while the candy is boiling; therefore, the concentration of sugar in the solution increases gradually. This increase in sugar concentration causes a decrease in vapor pressure, and the boiling temperature rises slowly. The recommended test for determining when a candy is done is to boil the solution to the correct final temperature (Table 4). This temperature is correlated with the concentration of sugar, and thus a thermometer is used to indicate when the correct sugar concentration has been reached.

Crystalline candies vary slightly according to the type of candy, but most have a sugar concentration of about 80 percent or slightly greater. This concentration is achieved when the boiling temperature reaches 112°C (234°F). A slightly higher temperature means a higher concentration of sugar and a firmer candy; conversely, a lower temperature yields a softer one.

Acid, usually in the form of cream of tartar, commonly is an ingredient in crystalline candies. During the boiling period, acid promotes **inversion** (hydrolysis) of some of the sucrose molecules. The end products of inversion are equal amounts of glucose and fructose, referred to collectively simply as **invert sugar**.

The extent of inversion accomplished by the acid during the boiling period is directly related to the rate of heating. A candy that is boiling slowly undergoes more inversion

Inversion
Formation of invert sugar by either boiling a sugar solution (especially with acid added) or adding an enzyme (invertase) to the cool candy.

Invert sugar
Sugar formed by hydrolysis of sucrose; a mixture of equal amounts of fructose and glucose.

Table 4 Final Temperatures and Approximate Concentrations of Sugar in Selected Crystalline and Amorphous Candies

Candy	Type	Final Temperature (°C)	Approximate Concentration of Sugar (percentage)
Fudge	Crystalline	112	80
Penuche	Crystalline	112	80
Fondant	Crystalline	114	81
Caramels	Amorphous[a]	118	83
Taffy	Amorphous	127	89
Peanut brittle	Amorphous	143	93
Toffee	Amorphous	148	95

[a]The large amount of fat interferes with crystallization.

because it requires a longer time to reach the desired concentration of sugar than one boiling so vigorously that a large quantity of steam constantly is escaping from the candy.

This chemical change catalyzed by acid is significant in influencing the textural characteristics of the finished product. Extensive inversion causes crystalline candies to be somewhat softer than would be anticipated. Some inversion, however, is helpful in promoting a smooth texture. The mixture of different types of sugars (sucrose, glucose, and fructose) resulting from some acid hydrolysis makes it somewhat difficult for the crystallizing sugars to form the large aggregates that give some candies a sandy, gritty texture.

Inversion of sucrose by acid hydrolysis is but one of the means used to obtain a mixture of sugars and to promote a smooth texture in crystalline candies. Corn syrup actually is a mixture of carbohydrate compounds derived by hydrolyzing cornstarch. All corn syrups contain glucose and maltose plus some larger glucose polymers, but those made with high-fructose corn syrup (HFCS) also contain fructose because of the enzymatic conversion of some of the glucose during production. Any of the corn syrups will enhance the texture of crystalline candies because of the mixture of sugars they provide. The distinctive shapes of the crystals of different kinds of sugars interfere with ready alignment of crystals into large aggregates.

Fat also interferes with aggregation of sugar crystals in the finished crystalline candies. When cream is used in preparing candies, its fat is useful in promoting a smooth texture. This is one of the reasons that fudge is more likely to have a smooth texture than is a simple fondant made with water as the liquid and with no added fat. Not only is fudge commonly made using cream, but it always has a significant amount of fat from the chocolate in the recipe (chocolate is at least 50 percent fat). Traditionally, some butter is added to crystalline candies at the end of the boiling period. This addition has two advantages: it promotes a fine texture by interfering with crystallization, and it enhances flavor.

Crystallization. A key factor in crystalline candy making is control of crystallization. When the boiling candy is removed from the heat, the solution is saturated. No more sugar could be held in solution at that temperature, but all that is present is in solution and not in crystals. This is a stable arrangement. As the solution cools, however, the amount that theoretically can be in solution is reduced. For example, 669 g of sugar can be dissolved in 100 milliliters of water at 115°C (239°F), but only 487.2 g can be dissolved at 100°C (212°F) and 260.4 g at 50°C (122°F).

Interestingly, it is possible to cool a solution that was saturated at the end of the boiling period without precipitating the crystals immediately. If considerable care is taken to prevent crystal formation, crystalline candies can be cooled to about 45°C (113°F) while maintaining all of the sugar in solution. At this point, the cooling syrup is quite viscous, and the dissolved sugar greatly exceeds the quantity that theoretically can be in solution. It is a supersaturated solution and is very unstable. Almost twice as much sugar is in solution as theoretically can be dissolved at the same temperature. The excess sugar will start to crystallize promptly if any nuclei for crystallization are provided.

The goal in making crystalline candies is to achieve a fine, smooth texture by controlling crystallization. Absolutely no nuclei should be available while the candy is cooling to the desired degree of supersaturation [a temperature of about 45°C (113°F)]. Care should be exercised to avoid the presence of sugar crystals on the sides of the pan in which the candy is cooling. Nothing should touch the surface at any time during the cooling period, and no movement should disturb the candy. Even adjustment of a thermometer in the cooling candy can be sufficient to start crystallization too soon.

When the desired degree of supersaturation is reached, beating is initiated to provide constant disruption of the crystals as they attempt to aggregate (Figure 3). The combination of the viscous solution at about 45°C (113°F) and the agitation results in crystallization of the excess sugar in such small aggregates that the finished product has a smooth, almost velvety feel on the tongue. This is the ideal situation.

If something happens to start crystallization before the candy achieves the desired degree of supersaturation, it is important to begin beating immediately and to continue until the candy solidifies. This agitation is essential to keep breaking aggregations into as small units as possible so that the texture will be fairly smooth when finished. Even with this effort, the texture will not be as smooth as when crystallization is avoided until the candy has become highly supersaturated (Figure 4).

When careful techniques to achieve supersaturation are combined with adequate beating, excellent crystalline candies can be produced. In addition, the presence of a variety of sugars and other interfering agents enhances quality by promoting a smooth texture. By selecting a recipe with interfering agents (cream of tartar and fat-containing ingredients) and by boiling candies containing an acid at a moderate rate to achieve an appropriate amount of inversion, candy makers can help ensure successful crystalline candy products.

Ripening. Although they appear to be in a permanently solid form, crystalline candies actually are quite dynamic in nature. Continual dissolution and recrystallization of sugar crystals occur in these products during storage. When viewed under a microscope, the structure reveals some liquid (referred to as **mother liquor**) as well as many crystals in various-sized aggregations. As crystals dissolve into the mother liquor, other crystals form on existing aggregates. The small, individual crystals are fairly susceptible to going into solution and ultimately being recrystallized. Although this process is rather slow, it is relentless in causing a gradual change during storage. These changes are referred to as the **ripening** of the candy.

Mother liquor
Liquid in a seemingly solid crystalline candy.

Ripening
Changes that occur in crystalline candies when they are stored.

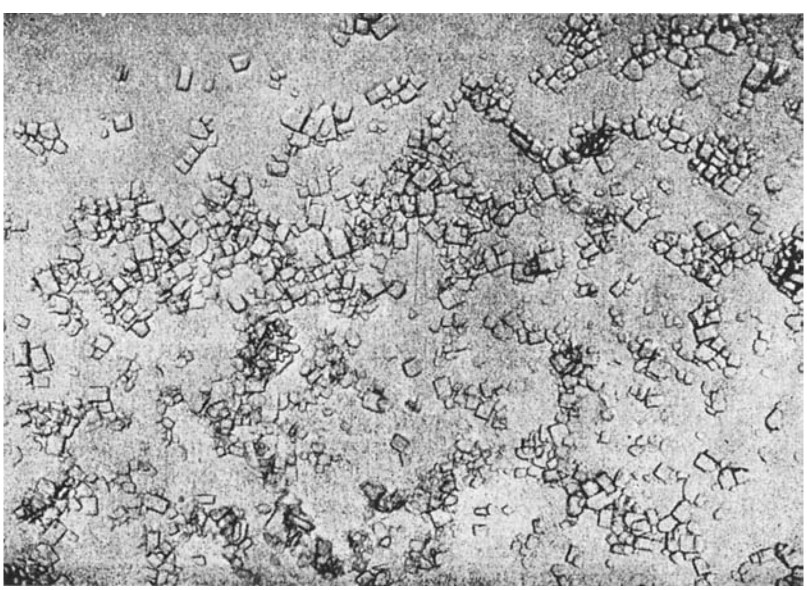


Figure 3 Crystals from fondant cooked to 113°C (235°F) and cooled to 40°C (104°F) before being beaten until the mass was stiff and could be kneaded (X200).

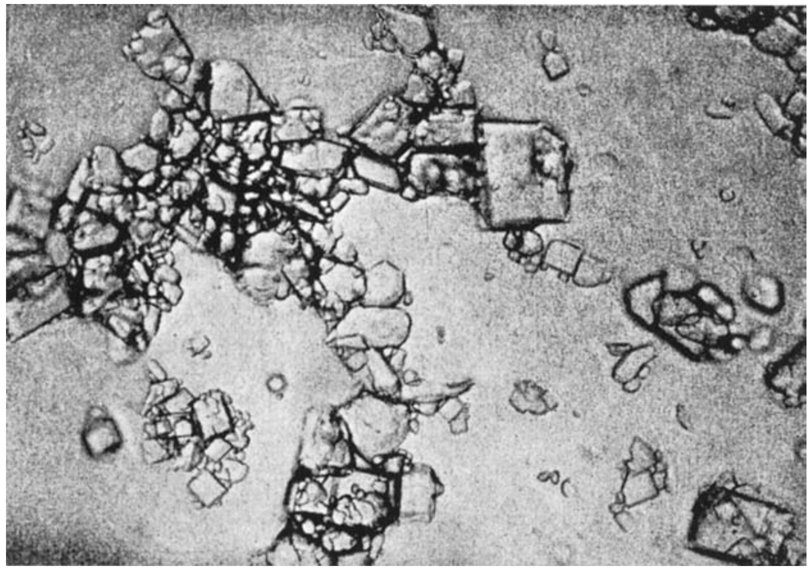


Figure 4 Crystals from fondant boiled to 113°C (235°F) and then beaten immediately and continuously until the mass could be kneaded (X200).

During the first few days of ripening, there is a bit of softening and smoothing of the texture as equilibrium is established. However, the texture of ripening candies gradually becomes coarser during storage. This developing grittiness is due to the increasing size of the crystal aggregates. Because there is no agitation while the new crystals are forming, they are attracted to existing crystals rather than forced apart mechanically. This transition is detectable over several days of storage. An adequate amount of interfering substances in the recipe helps retard undesirable changes caused by ripening (Figure 5).

Chocolates with cream centers are popular commercial candies that require several days of ripening before reaching their optimum texture. The difference between these soft-centered

Figure 5 Crystals from fondant in Figure 3 after 40 days of storage show significant increase in crystal size (X200).