TEXTURE AND CRYSTALLIZATION CONTROL IN RAISINS

ABSTRACT
Upon protracted storage of raisins a crystalline material can develop on their surface, especially at higher moisture levels. A method of controlling this formation was developed, which consisted of subjecting the raisins to a mild heat-treatment. This heat-treatment procedure also had a tenderizing effect on raisins, making them noticeably softer. Other factors were studied that affected raisin texture during storage with bran flakes. Raisin desiccation rate was found to be affected by storage temperature, pressure and coatings. Paraffin coating had the most pronounced effect. Protein coatings of solubilized soy protein or egg albumen followed by heat-denaturation also significantly reduced moisture loss from raisins stored with bran flakes.

INTRODUCTION
RAISINS are an energy rich food that was originally simply eaten out-of-hand. However, because of their small convenient size, they are a natural for formulating into bakery products, where they add a definite richness. Their use has been expanded even further to incorporation into dry cereals where, however, new problems are introduced. When 16% moisture raisins are packaged in a sealed container with 3% moisture bran flakes the system equilibrates and desiccation of the raisins occurs, the raisins become hard and chewy, and the bran flakes lose some of their crispness. Watters and Brekke (1961) studied methods of retarding this moisture transfer by dipping the raisins in various compounds. Of those tested, the only material they found that had a significant effect was beeswax. Coating with beeswax has been used commercially, but with only moderate success due to the difficulty of obtaining a uniform coating and the friability of the wax. Since raisin hardening is still a problem, especially when incorporated into the new granola-type cereals, a study was needed to determine methods of producing a softer texture raisin, by either developing a method to tenderize raisins or to control their moisture loss rate.

Also, during protracted storage of raisins a crystalline material often develops on their surface. This material seems to appear more rapidly on higher moisture raisins and those made from overly mature grapes. These surface crystals detract from the raisin appearance and make them less acceptable to the consumer. Thus, a treatment is also needed to control and minimize the surface crystal occurrence.

There are two main ways to control adverse texture development in stored raisins: (1) treating the raisins to make them initially more tender; and (2) controlling their moisture content. Moisture loss during storage can be controlled by varying the storage conditions, or by coating the raisins to retard their moisture loss. Each of these areas will be discussed independently, including a newly developed heat-treatment that both softens the raisins and inhibits sugar crystallization.

MATERIALS & METHODS
MIDGET RAISINS which are used in raisin-bran cereal, were obtained from a commercial packer. Raisin-bran was prepared by mixing to gether 105g of 40% bran flakes (aw = 29) with 35g raisins (aw = 59) in a liter container and sealing. Heat treatment was performed in a large electrically heated oven. Microwave heating was accomplished by spreading 250g of raisins on a Lucite tray and placing it in a Radartech Raderange Mark III oven, operating at 2450 megacycles and 800 watts. After heating, the raisins were put in a glass container, which was sealed and packed in an insulated carton. A polarization microscope with adjustable heat stage was used for crystal examination and melting point determinations.

All of the coatings were applied by dipping the raisins into the respective liquid or dusting them with the powders. Protein coatings were applied by dipping the raisins in the protein solution, allowing them to drain for 1 min and finally denaturing the protein by heating in a 115°C dehydrator oven for 4–5 min. The protein dip solutions were prepared by dissolving 40g spray-dried egg white powder or 40g solubilized soy protein in 60 ml water. Pressure packaging was carried out in a steel container 5 cm diameter by 17 cm long with a valve attached for pressurization and monitoring.

Moisture was determined by the AOAC vacuum oven procedure (1971). Texture measurements were made using a Kramer Shear Press equipped with a 1361 kg ring which determines the force required to push a series of metal plates through 90g of raisins (Kramer and Backinger, 1959). The shear press was operated at a plunger speed of 4, which required 60 sec for full stroke; also, the standard shear-compression box was used as the test cell. Color measurements were made using a Gardner Color Difference Meter.

RESULTS & DISCUSSION
Heat-treatment
A heat-treatment process was developed by Nury et al. (1964) and Bolin et al. (1965) for retarding the crystallization hardening that occurs upon storage of ground raisins. After a series of exploratory experiments it was found that heating also had an effect on the texture of whole raisins. After raisins had undergone a certain minimal heating, they had a softer texture than untreated ones (Table 1). The mildest heat-treatment that gave a consistently significant effect was heating for 48 hr at 49°C. Raisins thus treated had a softer texture immediately after heating as well as during protracted storage in raisin-bran (Fig. 1). During storage, both the heat-treated and control raisins lost moisture at the same rate, but the heated raisins remained softer. Heat-treated raisins at 11% moisture had the same texture as the control at 15% (Fig. 2). Panel evaluation also indicated the effectiveness of the heat treatment. When treated and untreated 11% moisture raisins

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Moisture (%)</th>
<th>Shear force (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>11.0</td>
<td>570</td>
</tr>
<tr>
<td>38</td>
<td>10.9</td>
<td>580</td>
</tr>
<tr>
<td>54</td>
<td>10.8</td>
<td>470</td>
</tr>
<tr>
<td>71</td>
<td>11.4</td>
<td>410</td>
</tr>
<tr>
<td>88</td>
<td>11.4</td>
<td>460</td>
</tr>
</tbody>
</table>
were submitted in pairs to a panel, 87% indicated the heat-treated raisins had a softer texture.

In addition to developing a softer texture, the heat-treatment also retarded the formation of excessive crystals on the raisins. Visual examination of heat-treated raisins, stored at 22°C for 10 months, revealed no evidence of crystal formation. Microscopic examination of the raisin surface revealed a few scattered large individual crystals. These crystals melted at 86°C and 146°C, indicating that they were glucose monohydrate and anhydrous glucose, respectively. These crystals did not adversely affect texture.

In contrast, after 10 months storage, untreated raisins had a prodigious amount of crystallized surface material which extended through the fruit skin into the pericarp (Fig. 3). Miller and Chichester (1960) determined by thin-layer chromatography that raisin "sugar" consisted of glucose, fructose and tartaric acid, but they did not determine the crystalline form of these sugars. Our physical examination revealed a large mass of crystals in an invert syrup matrix. The bulk of the crystals was judged to be glucose monohydrate by their characteristic hexagonal angular formation and melting point, 86°C. These crystals are very thin and fragile and break easily. The matrix also consisted of a few other small thin needle-like crystals that melted at approximately 160°C, which is indicative of tartaric acid. No anhydrous glucose crystals were detected. The mass of crystal formation occurs on the large ridges of the raisins. This could be due to a greater permeability of the skin in this area to the sugar solution. According to Possingham (1972) the surface of a raisin is composed of a network of intermingled wax platelets. Possibly, upon drying, the formation of the obtuse angles of the skin causes a stretching and separation of the wax platelets, thus allowing the solution of sugars to pass through the skin to the outer surface in these areas. On the surface, the water moisture is readily evaporated, leaving behind a saturated sugar solution which easily crystallizes in the presence of a few small seed crystals.

Heat-treating caused a slight darkening in the raisins. This was detected visually as well as from reflectance measurements. The untreated raisins gave a reflectance (L) of 17.2 compared to a reading of 14.8 for the heat-treated product, which indicates a small, but visually noticeable difference. Also, the heat-treated raisins had a moist appearance.

Microwave heating was also investigated to determine its applicability to the heat-treatment process, because it could greatly shorten the treatment time. Raisins heated quickly in a microwave field but only those that remained warm over a period of hours became softer. After 17 sec in the microwave oven the raisins reached 60°C; however, they cooled to less than 37°C after 4 hr storage. The microwave heated product did not undergo any softening. By increasing the time in the oven to 26 sec the raisins reached 76°C, and after 4 hr of storage they were still over 40°C. These raisins were softer, giving a shear force of 100 kg, less than the untreated or slightly heated samples. This indicates that a short heat treatment is not adequate. The product must be held about 4 hr at an elevated temperature to allow the crystalline matrix to dissolve and be dispersed within the raisin. After heating there are, evidently, no seed crystals available to initiate crystallization.
Storage conditions

The mechanism by which moisture is lost from raisins consists of the water molecule diffusing through the raisin to the surface where it is then vaporized into the surrounding atmosphere. Rate of diffusion (D) is temperature dependent, as indicated in the equation from Fick's and Stoke's law:

\[ D = \frac{R}{6N\eta} T \]

The values inside the parentheses are constants for a given system, \( T \) is absolute temperature and \( \eta \) is the viscosity of the medium. The equation indicates that a temperature decrease, which in turn results in the medium viscosity increase, would result in a decrease in the diffusion coefficient and rate of diffusion.

To determine to what extent storage temperature influences water migration from raisins, a series of raisin-bran samples was prepared and stored at different temperatures. Moisture analyses indicated that at higher temperatures, equilibrium condition is reached within about 2 wk, with a rapid initial loss of water to the flakes (Fig. 4). As the storage temperature is lowered, the loss rate decreases. Conversely, the bran absorbs more moisture at the warmer temperatures (Fig. 5). Lowering the storage temperature also affects the vapor pressure. Lowering from 21°C to -10°C causes a calculated tenfold reduction in vapor pressure; this also contributes to reducing the rate at which equilibrium conditions are obtained. Therefore, raisin-bran stored at lowered temperatures exhibits a reduced moisture transfer rate.

The rate at which an equilibrium vapor pressure is reached in an enclosed system containing two different materials is not only dependent on temperature, but is influenced by pressure. As pressure increases, the time to reach equilibrium increases. Experimental lots of raisin-bran consisting of 18% moisture raisins and 2% moisture bran flakes were stored in metal cylinders. The pressure inside the cylinders was increased to 135 psi. After 12 days storage at 21°C, the moisture content of the raisins under pressure had dropped to 10.8%, compared to 9.9% in the control. Pressure packaging at 135 psi does significantly retard the rate of loss of moisture from raisins. Obviously, however, this type of packaging would be impractical.

Coating

Various coating materials were tested, including sugars, flour, starches, sorbitol, glycerol and agar, but with marginal or no effect. Paraffin coating, however, proved to be a good moisture barrier. Raisins dipped in warm paraffin lost only 1.5% moisture after 2 wk storage, compared to 7% for the controls. If the dip solution was diluted to 10% paraffin with vegetable oil, the loss increased to 3.5%. Landerman et al. (1960) indicated that moisture will not migrate through a 0.8 mm thick sheet of solid paraffin. Paraffin is difficult to apply evenly as a thin coating. It is brittle at cooler temperatures and the coating can easily develop cracks during commercial handling. Beeswax and paraffin have similar properties.

Another material that retarded moisture loss was a protein coating, which was denatured after application. Raisins coated with either egg albumen or solubilized soy protein, had a significant reduction in moisture loss (Table 2). This treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raisin</td>
</tr>
<tr>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>Alubumen</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>17.8</td>
</tr>
<tr>
<td>Coated</td>
<td>18.2</td>
</tr>
<tr>
<td>Solubilized soy</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>16.9</td>
</tr>
<tr>
<td>Coated</td>
<td>16.4</td>
</tr>
</tbody>
</table>

\(\ast\) Significantly different than control at 0.01 level.
has the additional advantage of increasing the protein content of the product. The coating is about 0.1–0.2 mm thick, but could be made thicker if desired. Raisins coated with solubilized soy protein were sticky and would have to be dusted with starch or some other material to make them free flowing. The heat denaturation step is essential, both to remove excess water before it is absorbed into the raisin, and also to provide a more rigid moisture barrier. This coating gives a foamy brown appearance but does not detract from the normal raisin flavor.

Raisin hardening during storage under low humidity conditions can be minimized by a combination of heating, coating and low temperature storage. Heat treating makes the raisin initially softer and minimizes crystal formation; storing at lower temperatures and coating reduces the moisture migration rate.

REFERENCES


Ms received 1/16/76; revised 4/7/76; accepted 4/12/76.

References to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others which may also be suitable.

Presented at the 36th Annual Meeting of the Institute of Food Technologists, Anaheim, Calif., June 6–9, 1976.