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EFFECTS OF WATER QUALITY ON PHYSICO-CHEMICAL AND ORGANOLEPTIC  
CHARACTERISTICS OF SELECTED CANNED  
FRUITS AND VEGETABLES

by

Anita Kay Wilson

A dissertation submitted in partial fulfillment  
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Food Science and Technology

UTAH STATE UNIVERSITY  
Logan, Utah

1971



## ACKNOWLEDGMENTS

I am sincerely grateful and indebted to Dr. D. K. Salunkhe, Professor of Food Science and Industries, for serving as thesis director and for his invaluable guidance throughout my tenure at Utah State University, and also to Dr. Ethelwyn B. Wilcox, Chairman and Professor of Food and Nutrition, for serving as major professor.

Appreciation is expressed to committee members, Dr. Deloy Hendricks, Associate Professor of Food and Nutrition, Norman B. Jones, Associate Professor of Civil Engineering, and Dr. Frederick J. Post, Associate Professor of Bacteriology and Public Health, for advice in program and research planning and for review of the manuscript.

Special thanks are given to Drs. Deloy Hendricks and Arthur Mahoney, for advice in laboratory procedure and technique in the food and nutrition laboratory.

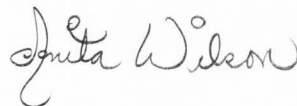
Acknowledgment is made to Dr. Donald V. Sisson, Associate Professor of Applied Statistics and Computer Science, for assistance in statistical analysis, to Dr. Bharat Singh, Assistant Professor of Food Science and Industries, for help in selection of laboratory procedures, to Dr. M. C. Cannon, Professor of Chemistry, for aid in interpretation of laboratory tests, and to organoleptic panel members for their faithful product evaluation.

I am grateful to the American Home Economics Association and the National Science Foundation for providing fellowships and to Stout State

University, Menomonie, Wisconsin, for granting a leave of absence to complete this work.

I wish to thank Perry Canning Company, Perry, Utah, and Del Monte Corporation, Franklin, Idaho, for providing sour cherries and green beans, respectively, and to the Geigy Chemical Company for providing EDTA used in this study.

Special gratitude is expressed to my husband, Richard, for his help and understanding and to my son, Mark, whose cheery smile provided incentive for completion of this degree.

A handwritten signature in cursive script that reads "Anita Wilson". The signature is written in dark ink and is positioned above the printed name.

Anita Wilson

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## ABSTRACT

Effects of Water Quality on Physico-chemical and Organoleptic  
Characteristics of Selected Canned  
Fruits and Vegetables

by

Anita Kay Wilson, Doctor of Philosophy

Utah State University, 1971

Thesis Director: Dr. D. K. Salunkhe  
Major Professor: Dr. Ethelwyn B. Wilcox  
Department: Food Science and Technology

The effect of processing water quality, specifically calcium and magnesium salt content (0-500 mg/l) and the addition of chelating agents (0-250 mg/l of aminopolycarboxylic acids, polyphosphates, hydroxycarboxylic acids or phytates), upon physico-chemical and organoleptic characteristics of canned Jonathan and Delicious apple slices, Montmorency cherries and Blue Lake green beans was investigated.

Physical determinations: shear values, turbidity of syrup or brine measured via light transmittance, Hunter color and color difference meter readings and internal can corrosion; chemical composition: pectin as calcium pectate, volatile reducing substances, total acidity, pigment determinations, nitrate-nitrogen values; and sensory measurements: texture, shape, flavor, aroma, color value and uniformity of product and color value and turbidity of product brine or syrup were ascertained. Analyses of variance,



Duncan's multiple mean comparison range tests and correlation coefficients were calculated when appropriate.

Use of hard water (300 mg/l) as a processing medium for canned apple slices and sour cherries decreased color and flavor acceptability but increased firmness and shear values. Excessive hardness toughened cherry epidermis making texture undesirable. Addition of 250 mg/l  $\text{CaNa}_2\text{EDTA}$  to Delicious apple slices canned in water containing 300 mg/l salts improved color and flavor while firmness was retained.

Delicious apple slices were firmer, had higher shear, nitrate-nitrogen and aroma scores and caused less detinning than Jonathan samples in all storage groups. As corrosion increased, nitrate-nitrogen, shear, firmness, flavor, aroma, and pigment values decreased. Color acceptability, reflectance, flavor and volatile reducing substances were higher and redness lower for Jonathan apple slices than Delicious samples stored at 35 and 75 F for 1 and 3 months, respectively, but not necessarily for samples stored at 100 F for 4 months. EDTA was ineffective in maintaining or improving Jonathan apple or Montmorency cherry quality, probably due to the acidity of these cultivars.

Apple and cherry quality decreased as storage temperature and duration increased from 35, 75 to 100 F for 1, 3 and 4 or 5 months, respectively, for all samples except Delicious apple slices with  $\text{CaNa}_2\text{EDTA}$ . EDTA did provide most color protection in sour cherries, and citric acid, best flavor and aroma scores, while commercial and tap water processed sour cherries showed most deterioration, but none were of acceptable commercial quality

after 5 month storage at 100 F. When comparing 1 month storage at 35 F with 3 months at 75 F, analyses of variance showed significant differences for every cherry characteristic measured except texture judged subjectively. All F values for apple storage variables were significant.

Blue Lake green beans canned using distilled water or with 250 mg/1 CaNa<sub>2</sub>EDTA had higher color and greenness values, less turbidity, generally better flavor and aroma, but lower shear, shape and firmness scores than tap or hard water or commercially processed green beans. Addition of 250 mg/1 ascorbic acid to hard water used to process green beans retained greenness, clarity of brine, flavor and aroma while reducing slough and splitting of pods, when stored 4 months at 75 F.

(114 pages)

## INTRODUCTION

The 180 million people in the United States use more than 300 billion gallons of water a day or about 1600 gallons per person per day (Ratzesberger, 1964). It has been estimated that by 1975, 2000 gallons per capita per day will be required. This is a particular problem in the western United States where population is increasing faster than in the rest of the nation (Harrison, 1960a). As an example, Utah's population increased 29.4 percent from 1950-1960; the estimates for 1980 predict a 59 percent increase. By 1980, Utah alone may need 24 percent more water than in 1960 and the state has already developed direct diversion of natural streamflow from rain and snow to maximum levels (Harrison, 1960b). Only about one-third of the irrigated acreage in Utah has an adequate water supply at the present time (Griffin, 1966), and it is agriculture and specifically irrigation which is and will continue to be the largest consumer of manageable water in the United States (Bishop, 1971).

Natural and industrial pollutants can make culinary water supplies unfit for good processing. Water in Utah and throughout much of the west contains substantial amounts of calcium, magnesium, iron, copper, sulfur and other minerals. Sodium, calcium and magnesium sulfates may give bitter flavors to processed fruits and vegetables. Calcium and magnesium chlorides cause hardness of water which toughens vegetables and adversely affects color and clarity, flavor and carbonation of canned and bottled

beverages. Iron and copper compounds combine with tannins in fruits and can cause blackening. Sulfur compounds cause detinning and corrosion of cans. They precipitate after polymerization and can cause scum and cloudiness in brine and syrup (Salunkhe and Chiang, 1971).

The present trend in consumer purchasing of fruits and vegetables is increased consumption of processed rather than fresh produce, and this trend is predicted to intensify. The Western states including Utah generally process a much smaller percentage of their crop than do the Eastern states (United States Department of Agriculture, 1968; Salunkhe et al., 1966). The major fruits produced in Utah are sweet and sour cherries, apricots, peaches, pears and apples (Nielson, 1964) amounting to a \$9-15 million industry according to Utah agricultural statistics in 1963. An expansion of the processing industry would benefit the fruit growers of Utah, particularly in the northern part of the state (Salunkhe et al., 1966). Nielson (1964) pointed out that since Utah has a limited fresh fruit market and home canning is declining in volume, processors are needed if the industry is to prosper. He included the example of sour cherries stressing that Utah can produce fruit of the quality produced in the leading cherry producing state, Michigan. Since Utah is close to the Pacific coast market and the Intermountain states market is increasing, demand should be great.

Quality of fruits and vegetables processed in hard-water areas such as those throughout much of the Intermountain West can be improved by the addition of chelating or sequestering agents to the canning water or to the product during processing. An investigation of leading chelating agents, such as

aminopolycarboxylic acids, phosphates and hydroxycarboxylic acids, on canned fruits and vegetables of different physico-chemical composition is needed.

Rapid detinning of cans used for processing fruits and vegetables has been encountered with increasing frequency. Products not previously considered problems have been involved. Water and/or food components, such as nitrate content, have been implicated, but research results are conflicting. More information is urgently needed concerning cause and mechanism of rapid detinning. Role of sequestrants in preventing this problem would be of interest.

Increased demand for canned, frozen and dried apple products has been noted in recent years, but no increase in cultivars adapted particularly for processing have been forthcoming. Between 1934-44, approximately 9 to 15 percent of the American apple crop was canned, frozen or dried (Smock and Neubert, 1950). Since 1960, about 25 percent of the crop has been processed; about 78 percent of the processed apples were canned in 1963 (Darymple and Feustal, 1965). Cultivars with firm texture, pleasing flavor and high acidity that yield white or light-colored products are desired. Red Delicious apples, the cultivar produced in largest numbers in the United States, is preferred by most Americans for eating. They are too firm in texture for some processed and cooked products, are low acid and tend to break up during preparation and processing. Techniques to improve the processing acceptability of the Delicious cultivar would be of value to the industry.

The objectives of this research project include investigation of processing water quality, specifically calcium and magnesium salt content and the addition of chelating agents (aminopolycarboxylic acids, phosphates,

hydroxycarboxylic acids and phytate), upon

1. physical properties: shear values, Hunter color and color differences meter readings, turbidity of brine or syrup measured via light transmittance, and internal can corrosion and detinning
2. chemical properties: pectin as calcium pectate, volatile reducing substances, nitrate-nitrogen, total acidity, and pigment determinations; and
3. organoleptic properties: texture, shape, turbidity of product brine or syrup, flavor, aroma, color value and uniformity of the product and color value of brine or syrup, of canned sour cherries, Jonathan and Delicious apple slices and Blue Lake green beans.

## REVIEW OF LITERATURE

### Role of Water in the Canning Industry

#### Quantity needs

Water is the lifeblood of the canning industry, pointed out James (1965) since foods are in many cases in contact with water from time of arrival at the factory until their consumption. Today there are over 2000 canneries in the United States and her territories processing over 1200 different canned items and combinations. In 1965, 765 million cases with over 27 billion tin and glass containers were packaged--227 million cases of vegetables, 124 million cases of fruit, followed in numerical value by 114 cases of fruit and vegetable juices (United States Department of Interior, 1968).

About twice as much water, 50 gallons per case of canned food (Ratzesberger, 1964), is used today as was used 20 years ago. This is due to increased emphasis on quality and rigid definitions of clean food, to increased interest in government buying agencies on plant sanitation, on more dust and dirt on products entering plants as a result of increased mechanical harvesting and finally by increased water conveyance in plants (Lopez, 1969). The uses of water in canning plants have been tabulated in percentages by the United States Department of the Interior (1968) as follows: cleaning food, 15; transportation, 10; product preparation, 10; packing medium, 6; container sterilization, 15; cooling medium, 36; and cleaning and waste fluming, 8.

Fruit and vegetable canning is seasonal, thus water demands may vary 100 fold among the months of the year (United States Department of Interior, 1968). Seasonal variability also makes waste disposal a problem since fluctuation in composition and volume makes efficient plant design difficult; furthermore canneries are usually situated in rural areas where sewage works are small (James, 1965). Ratzesberger (1964) emphasized that in 1964, waste disposal costs were \$0.0007 per case of food and would jump over the next few years to \$0.045; he recommended that waste disposal facilities be classed as a deductible business expense. Waste disposal is very important since average consumption of water in a canning plant is only 8 percent while 92 percent is discharged. Presently plants average reuse of 37 percent of their water intake (United States Department of Commerce, 1966). Statistics concerning international uses of water are summarized by Furon (1967).

#### Quality requirements

Quality of water for canning depends upon three factors: inorganic compounds, organic impurities and microbial content (Murray and Peterson, 1951). The United States Department of Interior in its 1968 report from the committee on water quality criteria stated that water quality deterioration can cause product deterioration. Excessive inorganic compounds in the water necessitate boiler water treatment, water hardness affects economical cleaning and product texture and other minerals can cause discoloration and poor flavor in foods. Recent work has shown a correlation between nitrate content of the water or food and rapid detinning of the can which leads to product unacceptability.



Organic impurities in the water cause flavor and odor problems while water with high microbial content is a public health hazard.

This thesis deals exclusively with the first quality consideration: the role of inorganic compounds in the water and its effect on canned fruits and vegetables.

Hardness is defined as the soap-neutralizing power of a water. Many substances will form an insoluble curd with soap, although the principal offenders are calcium and magnesium salts. Hard water is distributed widely throughout the United States and may be caused by natural accumulation of salts from contact with soil and geological formations or it may enter from direct pollution by industrial wastes or return flow from irrigation waters (McKee and Wolf, 1963).

If the carbonate and bicarbonate content of water is equivalent to or greater than calcium or magnesium levels, a calcium carbonate and magnesium hydroxide scale will form upon evaporation or heating. Acid removes this deposit; hence the term "temporary" or "carbonate" hardness (McKee and Wolf, 1963).

Sulfate and chloride compounds of calcium and magnesium form insoluble scales and are termed "permanent" or "noncarbonate" hardness. In arid and semiarid regions, sodium sulfate accumulates in drainage waters so rivers may carry high sulfate content (Collins, 1943). Utah river waters are of three basic salt types: calcium sulfate-magnesium chloride, calcium carbonate-magnesium bicarbonate, and sodium sulfate-potassium chloride. Average

dissolved solids in water withdrawn for public supplies in Utah varies from 250-450 mg/l (Thorne and Peterson, 1967).

Water from deep wells is frequently hard and sometimes corrosive, and although minerals may be present causing poor color, flavor and odor, this water is usually bacteria-free. Water from shallow wells (1-30 feet deep) is often bacterially contaminated and sometimes excessively soft; frequently surface water is polluted and variable in composition (Murray and Peterson, 1951). Today 24 billion gallons of water for canning comes from public water supplies, 20 billion gallons from ground sources, while 4 billion gallons is obtained from surface supplies (United States Department of Interior, 1968).

The canning industry has been concerned with water quality for many years. As early as 1915, Huenink and Bartow reported that both calcium and magnesium chloride and sulfates firmed canned beans and the effect increased with mineral concentration. In 1923, Bigelow and Stevenson described texture and color problems in vegetables when hard water was used. In 1938, Lancefield pointed out that carbonate hardness may cause surface scum and cloudiness in liquid of canned meats, fruits and vegetables. He recommended softening the water to below 50-70 ppm and suggested that the pH be no lower than 7.5. Water quality factors were defined by Weckel (1942) as acceptable flavor and color; clarity and freedom from turbidity, particles and sediment; inert in chemical properties; uniform in composition; acceptable bacteriologically; sufficient in volume; and acceptable in temperature.

Recently, Francis, Baker and Braswell (1971) warned that water impurities can cause processing problems and serious economic loss. McKee

and Wolf (1963) recommended that water used for food canning and freezing should be in the range of 50 to 85 mg/1 total hardness. Lopez (1969) recommended that water used for canning vegetables and fruits must be soft and free from any appreciable amount of organic material, obnoxious odor or taste. He stated, "Hard water is objectionable for boiler supply, for brine, for syrup, for all canning purposes." (Lopez, 1969, p. 16)

Problems involved with product acceptability are those concerned with texture, color and flavor of food, clarity of brine or syrup and can corrosion.

#### Water quality: Product texture

Much research has been completed on the textural properties of fruit and vegetables canned in hard and soft waters. In general, if the water is too alkaline, the product disintegrates (Lowe, 1955). If the water is too hard, it toughens vegetables making them difficult to process (Lopez, 1969).

Innumerable papers have reported toughening of peas and beans cooked, canned or blanched in hard water (Masters and Garbutt, 1920; Weckel, 1942; Bigelow and Stevenson, 1923; Heupke, Wenzel and Volker, 1944; Murray and Peterson, 1951; Salunkhe and Hamson, 1959; McKee and Wolk, 1963; and Lopez, 1969). It is felt that firming of vegetables rich in protein is due to formation of calcium and magnesium picrates or to precipitation of protein by calcium and magnesium salts (Simpson et al., 1955; Heupke, Wenzel and Volker, 1944).

Firming in hard water-canned products also has been reported for apples and tomatoes (Holgate and Kertesz, 1948; Collins and Wiley, 1967) and for sour cherries (Whittenberger, 1952). Calcium salts are added routinely to canned whole tomatoes to maintain firmness. Thickening of evaporated milk by salts was reported by Weckel (1942). Salunkhe and Hamson (1959) observed toughening of frozen vegetables when hard water was used for blanching while Simpson et al. (1955) noted that hardness tended to decrease water absorption when dehydrated fruits and vegetables were reconstituted. Green beans, asparagus, spinach, peas, parsnips, potatoes and squash have been shown to absorb calcium and magnesium ions from cooking water (Simpson et al., 1955; Noble and Halliday, 1937; Bryant and Jordan, 1948).

Collins and Wiley (1967) traced the path of radioactive  $\text{Ca}^{45}\text{Cl}_2$  in apple tissue. They reported that dipping or submerging slices in calcium solution allowed only surface penetration; processing slices in a calcium salt medium produced similar results and only outside tissue hardened. Use of vacuum-pressure while slices were submerged impregnated tissue evenly. Holgate and Kertesz (1948) also noticed uneven absorption.

#### Water quality: Product color and syrup clarity

Hard water was detrimental to color and clarity, flavor and degree of carbonation of bottled beverages (Weckel, 1942). Lack of clarity of brines and canned fruit syrups has been reported. Heavy metals have been implicated in the darkening of maraschino and glacé cherries. As little as 5 mg/1 copper will discolor them (Butland, 1952) and iron, aluminum, tin and a combination of

tannin, lead and iron all change the color (Kitson and Strachan, 1955; Atkinson and Strachen, 1936; Cohee and Nelson, 1951; Atkinson et al., 1952). Griswold reported in 1944 (a) that stannous and calcium chlorides lower palatability of home-canned Montmorency cherries. Beets form an insoluble white coating on the surface when canned in hard water or water with soluble oxalates (Murray and Peterson, 1951; Furia, 1964; Bigelow and Stevenson, 1923). Copper, iron and chromium cause a gray-green color in canned corn. Surface discoloration due to iron combining with rutin has been reported in sweet potato, yam, cauliflower, eggplant, asparagus, Brussels sprouts, and turnips (Furia, 1968; Davis et al., 1961; Cruess, 1958; Hernandez and Vosti, 1963). Iron also discolors potatoes (Smith and Muneta, 1954; Furia, 1964).

#### Water quality: Can corrosion and detinning

Internal can corrosion remains a persistent problem that has confronted the food canning industry throughout its history. Canned foods even though hermetically sealed and heat processed, undergo changes in both sensory quality and nutritional value on storage. Interactions between container and food result in discoloration and flavor impairment of food and liquid, loss in nutritional value, unsightly stains, corrosion or can perforation, and hydrogen gas evolution which may distend the can (Britton and Bright, 1960; Frazier, 1967) as well as leaving tin dissolved from the can within the food. The maximum storage life of a canned product may depend as much or more upon the stability of the container as upon the ingredients or food itself (Mitchell, 1955).

Since 1954 increasingly frequent outbreaks of rapid detinning of vegetable containers have occurred. Rapid detinning was found in foods that previously had not been considered problems.

Corrosion is an electrochemical reaction. For any given combination of metals the rate of current flowing is dependent on the properties of the electrolyte. Corrosion commences when the can is filled and continues rapidly during processing and for the first few days of storage until oxygen in the headspace is exhausted (Board and Elbourne, 1965). The oxygen combines with the container metal, the food or with nascent hydrogen formed by action of acid on metal (Cruess, 1958). After this time corrosion takes place anaerobically and proceeds slowly. Most acid foods packed in plain tin corrode by dissolving tin with little attack on the steel base. The tin forms the anode of the iron-tin couple and goes into solution at such a slow rate that protection is provided for 2 years or more. The anodic relationship of tin to steel is due to formation of tin complexes with fruit acids (Britton and Bright, 1960). When accelerating substances are present, tin removal is greatly hastened and food is protected only until most of the tin has been dissolved. Thereafter, hydrogen is produced at a rapid rate and a springer develops (Farrow, 1970).

Most of the active research centers on the role of secondary factors--cathodic depolarizers in the food, inhibitors and accelerators of tin or iron corrosion and complexing agents for tin and iron.

In tomatoes where detinning has become an increasing problem, it was noted that all tomatoes causing detinning in a lot came from the same field

and in each case from a field treated with mineral or organic fertilizers.

Tomatoes from such fields would detin containers completely within 6 months (Farrow, 1970). Nitrates from fertilizer were suspected.

Nitrate is not synthesized in plants; hence nitrate accumulation is the result of nitrate intake in excess of utilization. Nitrate absorption is influenced by soil nitrate level, transpiration and growth rate; utilization depends on growth rate (Hoff and Wilcox, 1970). They found that tomato fruit accumulated nitrate when the controlled environmental conditions combined high temperatures, high nitrogen fertilization level and low light intensity. Nitrate accumulation was preceded by low nitrate reductase activity and nitrate increase in leaves. This is in agreement with a review of nitrate accumulation in crops (Wright and Darison, 1964) who reported that in addition to the above three conditions, drought also favored nitrate storage. Effects reported have not been consistent, however, varying with species, age and soil type.

Sources of nitrates include animal excreta, crop residues, human waste, some industrial waste and decomposing plant and animal tissue (Hanway et al., 1963). Nitrates are water soluble and thus move with ground water; high nitrate levels are most likely to occur in water from shallow wells, but may be found in ponds and deep wells. Concentrations build up in water supplies by being leached through soil or by washing in from human, animal and industrial waste. Nitrate contamination of water is a bigger problem today than in the past because of greater use of nitrate-accumulating feeds, improper sewage disposal and water contaminated by animal waste.



Several studies have implicated nitrate in detinning. The amount of lead and tin dissolved in canned orange juice increased when well water containing higher concentrations of nitrate-nitrogen were used; sulfate had no significant effect on nitrate-stimulated detinning (Horio, Iwamoto and Oda, 1966). These authors recommended water containing not more than 1 ppm nitrate-nitrogen preferable for canned drink preparations. Johnson (1970) also reported that nitrates accelerate the corrosion rate of steel by increasing cathodic reduction rate in canned soft drinks. Farrow, Lao and Kim (1970) measured detinning rates in citrate-buffered nitrate solutions ranging in pH from 3 to 7. Detinning was extremely rapid below pH 5.2 to 5.5; for example, cans containing solutions containing 125 ppm nitrate and with a pH of 4.0 were completely detinned in 2 months.

Strodtz and Henry (1954) found corrosive action of nitrate towards tin was greatly dependent on pH of the media for canned green beans, mustard and turnip greens; they felt some corrosion factor other than nitrate was present. Lambeth, Fields and Brown (1967) found no significant relationship between addition of nitrate-nitrogen to canning brine and detinning in canned spinach. High temperature storage caused detinning; they believed corrosion accelerators besides nitrate to be present. In further study, Lambeth and workers (1969) found that spinach with high oxalate content produced by growing on low phosphorus, high nitrate and high potassium fertilized soil, caused detinning in excess of 60 percent in 9 months storage at 74-78 F. Potassium and oxalic acid were more related to detinning than nitrate content was.



The results of the nitrate studies do not agree and more work is needed on the effect of fertilizers on food used for canning, on nitrates in water and their effect on canned products and on other corrosion accelerators.

Sugars, anthocyanins and canning procedure have hastened detinning. Cheftel, Monvoisin and Swirski (1955) found caramelization products in fruits accelerated corrosion, particularly if the caramel was formed from glucose. Sucrose-based caramel did not show this effect. Britton and Bright (1960) reported that anthocyanins were less effective detinners than once believed. Alkaline water or water containing chloride, sulfur or sulfur compounds and copper have been implicated (Weckel, 1942; Hartwell, 1951). Corrosion accelerators in fruit juices and carbonated beverages include copper, sulfur dioxide, nitrate and some azo dyes (Alderson, 1970).

Vacuum closing and limited headspace slow corrosion because they limit oxygen. However large headspace is essential to prevent can distention in foods favoring can springer formation (Kohn and Fix, 1956; Bauernfeind, 1953; Cruess, 1958; Desrosier, 1963). Preheating or blanching helps drive air from the tissues as does a long exhaust period. Sealing in inert gases, although used presently for dry foods may show promise (Cruess, 1958). Corrosion inhibitors in canned beverages include the antioxidants, ascorbic acid and stannous chloride, as well as any process which limits oxygen in the can (Alderson, 1970).

#### Tin toxicity

Although most American studies have shown no danger of tin toxicity from canned foods, even those held at elevated temperatures (Calloway and

McMullen, 1966; Dickenson and Raven, 1962), some cases have been reported. Severe gastrointestinal illness was reported after consumption of punch containing 2000 mg/1 tin dissolved from a retinned milk can (Warburton et al., 1962) and Japanese workers reported poisoning from canned orange juice (Horio, Iwamoto and Oda, 1966). They also reported increased lead solution in juice with high nitrate content and subsequent rapid detinning.

### Sequestering Agents in Food Processing

The differentiation between chelating and sequestering agents is not clear. A chelating agent has been defined as a compound which inactivates a metallic ion by making it an integral part of an inner ring structure; a sequestering agent, a compound that will inactivate a metallic ion by forming a water-soluble complex in which the metal is held in nonionizable form (Smith and Muneta, 1954). Sequestration consists of:

suppression of a particular property or properties of a metal in solution, without the removal of that metal either into another phase nor its concentration into a particular portion of the original phase, while at the same time, the agent used for the purpose of this sequestration must not introduce any new factor, reaction or characteristic which makes the system unsuitable for the original purpose. (Smith, 1959, p. 3)

Since all sequestrants of practical value in the food industry are chelating agents, the terms will be used as synonyms in this discussion.

Interactions involving metallic ions in foods and beverages can be divided into two classes: reactions catalyzed by metals and reactions in which insoluble metal salts are formed. In both cases the function of a sequestrant is

to reduce free metal ions so no undesirable reaction occurs (Chaberek and Martell, 1959). The action of chelating agents is graphically described by Sawyer and McCarty (1969) as follows:

These substances have the ability to seize or sequester metal ions and hold them in a clawlike grip (the word is from the Greek, Chele, meaning claw). Like a claw a chelating molecule forms a ring in which the metal ion is held by a pair of pincers so that it is not free to form an insoluble salt. The pincers of a chelating molecule consist of "ligand" atoms (usually nitrogen, oxygen or sulfur), each of which donates two electrons to form a "coordinate" bond with the ion. (Sawyer and McCarty, 1969), p. 35)

Sequestrants tie up trace metals that catalyze oxidative breakdown of foods and thus can improve color, flavor and texture of foods (Sanders, 1966). They prevent formation of insoluble metal salts which cause turbidity and other quality deterioration (Chaberek and Martell, 1959).

For chelation to occur, two general conditions must be satisfied: first the ligand must have proper steric and electronic configuration in relation to the metal being complexed. For example, calcium, magnesium, copper, iron and zinc have square planar bond angles. Hence octahedral and tetrahedral ligands would be receptive to chelation of these metals. In the process of chelation, however, modification of natural bond angles may occur to permit ring formation; bond length and reactivity may change.

The second condition to be satisfied is that of the surrounding milieu, such as pH, ionic strength and solubility, which must be conducive for chelation. Competition between metals for position within a complex occurs. Chelation is an equilibrium process and rate depends upon stability constants (Furia, 1964; Furia, 1968; Dwyer and Mellow, 1964).

The particular sequestrant chosen depends upon these factors and also upon its proven safety in foods, other chemical and physical characteristics

affecting palatability, and cost of the additive (Furia, 1968). Examples of chelating agents include polycarboxylic acids, hydroxycarboxylic acid, polyhydroxy compounds, polyphosphoric acids, amino acids, and various protein and protein degradation fractions (Furia, 1964). All these agents react with alkaline-earth and heavy metals. Traditionally, hydroxy acids often have been used because of their low toxicity, ease of assimilation into products and the pleasant tart flavor they provide (Chaberek and Martell, 1959), although recently aminopolycarboxylic acids and various phosphates are assuming importance (Sanders, 1966; Furia, 1968). Often two chelating agents work well together where one becomes synergistic in the reaction of the other (Furia, 1964; 1968).

#### Ethylenediaminetetraacetic acid

Ethylenediaminetetraacetic acid (EDTA), a colorless, odorless, tasteless sequestrant, that chelates a larger variety of metals than most other agents has been investigated intensely. It is a hexadentate molecule; thus it forms a very stable ring. Zinc, iron, copper, bismuth, and cobalt EDTA-chelates are stable in acid; calcium chelation with EDTA increases with pH and is maximum above pH 8.5 (Furia, 1968). EDTA chelates iron preferentially (Smith and Muneta, 1954).

Since the compounds formed in hard water are soluble, nonionic compounds, the hardness is removed without precipitate formation. EDTA works at any temperature, is effective indefinitely and water requires no removal of precipitate after softening by this technique. Its storage life is excellent wet or dry at any pH (Bernsworth, 1950).

Both disodium EDTA ( $\text{Na}_2\text{H}_2\text{EDTA}$ ) and calcium disodium EDTA ( $\text{CaNa}_2\text{EDTA}$ ) have been approved by the Food and Drug Administration as non-GRAS food additives (Sanders, 1966) and in 1969 were permitted in 32 different foods as compared with approval for 21 products in 1964 (Furia, 1964; Anonymous, 1969). Since 1935, EDTA production has grown from zero to over 10 million pounds per year (Chaberek and Martell, 1959).

EDTA has prevented after-cooking darkening of pre-peeled potatoes (Smith and Muneta, 1954; Greig and Smith, 1955); surface darkening of sliced beets (Clark and Moyer, 1955); gray-green canned corn contaminated with trace metals; surface darkening of sweet potato, yam, cauliflower, eggplant, asparagus, Brussels sprouts and turnips; browning of apples and pears when combined with other antioxidants and stabilized vitamin preparations, fats, oil and salad dressing (Furia, 1968). EDTA improved sensory acceptability of sweet cherries and apricots canned in hard water (Chiang, 1970). Chaberek and Martell (1959) reported that EDTA-wash aided in removing heavy metal base insecticides from fruits and vegetables, facilitated effectiveness of alkaline peeling baths and prevented precipitation in jelly, shellfish and beverages. EDTA is used in canned shrimp, sandwich spreads, potato salad, canned beans, soft drinks and mayonnaise to prevent discoloration, off-taste and rancidity, and as an antigushing agent in beer (Sanders, 1966). Ascorbic acid in tomatoes and fruit juices was protected by adding EDTA salts early in the processing operation (Niadas and Roberts, 1959). Sistruck and Cash (1968) also reported EDTA protected ascorbic acid in frozen strawberries, but it did not prevent color loss.

No attempt will be made here to review the literature on the safety of EDTA; however, a report by FAO, WHO in 1967 stated:

CaNa<sub>2</sub>EDTA is very poorly absorbed from the human gut. The compound is metabolically inert and no accumulation in the body has been found. A vast clinical experience in its use in treatment of metal poisoning has demonstrated its safety in man. Long term feeding studies in rats and a one-year study in dogs have provided no evidence of interference with mineral metabolism in either species. Adverse effects on mineral metabolism and nephrotoxicity were seen only after parenteral administration of high doses. (FAO, WHO, 1967, p. 44)

An extensive bibliography is included in the above report. CaNa<sub>2</sub>EDTA is preferred to Na<sub>2</sub>H<sub>2</sub>EDTA as a food additive since under certain circumstances, Na<sub>2</sub>H<sub>2</sub>EDTA complexes with calcium in the body. Thus it may not be used in excess of 500 ppm and only if no excess of the compound remains in the food.

### Phosphates

Polyphosphates are commonly employed in industry as water softeners because they bind cobalt, copper and iron very strongly and calcium and magnesium quite well (Post et al., 1968). Commercially the most important polyphosphates include pryophosphate, tripolyphosphate and glassy metaphosphates. Polyphosphates are unstable, particularly at elevated temperatures and in the presence of calcium and magnesium, making them less desirable than EDTA. They are used extensively in boiler compounds, however, because they have been known longer and are less expensive than EDTA salts.

Sodium hexametaphosphate (Na-HMP) has a particularly high degree of surface activity. When added to hard water it has been found to tenderize peas and facilitate removal of pericarp of peach fruit (Salunkhe and Hamson,

1959). Tenderness is facilitated because insoluble calcium pectate gels cannot form in plant cells due to complexing of calcium with phosphate (Holmquist, Schmidt and Guest, 1948).

Pyrophosphates and  $\text{Na}_2\text{H}_2\text{EDTA}$  proved most effective in preventing after-cooking darkening of white potatoes (Furia, 1968) and caused no undesirable side effects. In fact both of these compounds improved texture of potatoes and increased shelf life of the fresh product by reducing greening and increasing mold resistance (Greig and Smith, 1955; Post et al., 1968).

Generally chain polyphosphates chelate most strongly and are the most stable particularly if chains are long, ring phosphates are second in effectiveness and orthophosphates have no activity (Post et al., 1968), although orthophosphoric, as well as citric and malic acids, were reported by Griswold (1944b) to improve color, but not texture or flavor, of canned applesauce.

#### Hydroxycarboxylic acids

Hydroxycarboxylic acids are thought to have a threshold effect in addition to true chelation, probably due to some crystal-liquid interface coordination (Smith, 1959).

Citric acid is a leading sequestering agent (Sanders, 1966; Arnold, 1970). When combined with antioxidants, it preserves color of fresh and frozen fruits, prevents pinking of canned pears and banana puree, and improves color in soft drinks and other foods and beverages (Arnold, 1970; Furia, 1968). Although citric, acetic and hydrochloric acids prevented darkening of cooked potatoes, they formed a tough unpalatable outer layer (Greig and Smith, 1955).



Citric acid helped to retain color of strawberry fountain syrup, but ascorbic acid was not effective in stabilizing a series of seven fruit juices when added in the ratio of 50 mg/100 ml juice (Nebesky et al., 1949). Citric acid added tartness to the product; Buch and workers (1956) found that addition of 0.1 percent citric acid to applesauce gave a pleasant tartness but 0.2 percent was excessively sour.

Pitted sour cherries retained quality when frozen in sugar syrup containing ascorbate but not in dry sugar. Saurkraut high in naturally occurring ascorbic acid retained better color than samples low in the acid. Hope (1961) used ascorbate to control apple browning. Addition of 300 mg/lb of fruit controlled browning, reduced headspace oxygen and increased nutritive value of fruit even when apple halves were canned without oxygen removal. Isoascorbic acid and sodium isoascorbate were not as effective as ascorbic acid. Ascorbic acid combined with EDTA showed promise. In apples, 1000 ppm ascorbic acid was required to prevent browning, but when combined with  $\text{Na}_2\text{H}_2\text{EDTA}$  only 250 ppm of each were required. Levels of up to 1000 ppm  $\text{Na}_2\text{H}_2\text{EDTA}$  alone were not effective (Furia, 1968). Ascorbic acid content was also related to color quality of frozen strawberries (Wrolsrud et al., 1970).

#### Other sequestrants

Calcium phytate has been reported to prevent discoloration of candied fruits by sequestering iron and copper (Kitson and Strachan, 1955; Butland, 1952; Cohee and Nelson, 1951). Markakis, Livingston and Fellers (1957) found that thiourea, propyl gallate, citric acid and quercetin were effective in



maintaining color of strawberries canned with short-time, high-temperature processing but that phosphates and EDTA were not beneficial and ascorbic acid was detrimental to pigment retention.

## METHODS OF PROCEDURE

Apples, cherries and green beans were canned during 1969 and 1970 using commercial methods. Products were processed in waters of varying mineral combinations and concentrations to simulate hard water conditions. Polyphosphoric acids, EDTA compounds, hydroxycarboxylic acids and calcium phytate were added to some cans to sequester metal ions. All canning was completed in the Utah State University food processing laboratory.

### Selection and Preparation of Samples

#### Apples

Jonathan and Delicious apples, Pyrus malus, from the 1969 crop at the Utah State University horticultural farm, Howell Field Station, North Ogden, Utah, were selected for this study. They were stored at 35 F and 80 percent relative humidity until processed within 1 week after harvest.

Initial studies on methods of slicing, filling and processing were conducted. Based on this work, apples in the 1970 study were randomized, peeled, cored and sliced into 12 equal slices with a combination corer-slicer, and slices were packed at random into commercial 2 1/2 cans. Three hundred g of fruit and 350 ml of syrup were used per can. Cans were exhausted and sealed with 20 lbs pressure using a Pacific No. 1 semi-automatic sealing machine processed in boiling water for 20 minutes and cooled in running cold water for 30 minutes.

Four salts (calcium chloride, magnesium sulfate, ferric sulfate, and cupric chloride) were used at 14 concentrations varying from zero to 2000 mg/1, based on net fluid content of the can. Distilled and tap water samples were also used. Processing was completed in both C enamel and plain type L tin cans and lids.

Various food additives were added to distilled, deionized water containing 200-250 mg/1 total calcium and magnesium salts. The purpose was to evaluate their effectiveness as water softeners and their effect in preventing oxidation of canned apples thus simplifying the canning operation by eliminating blanching and soaking steps that decrease flavor, particularly in low-acid Delicious samples, and lead to mushiness in Jonathan apples. Additives included disodium hydrogen EDTA, calcium disodium EDTA, magnesium EDTA, calcium phytate, citric, ascorbic and malic acids, sodium hexametaphosphate and pyrophosphate, aluminum sulfate and pectins.

Jonathan and Delicious apples were chosen for the main investigation in 1970. The best water variables from the 1969 study were chosen for further work and are included in Table 1. Plain type L tin plate cans with enameled lids were used since excessive corrosion of plain lids was noted (Figure 1). After processing cans were divided randomly within treatment lots into three storage groups and stored at 35, 75 and 100 F until analysis after 1, 3 and 4 months, respectively, in an attempt to simulate conditions around the world and to determine if any treatment was effective in preventing high temperature deterioration.

Table 1. Water variables chosen for canning syrup and brine of apples, cherries and green beans

Product	Water	Mineral Level* total mg/1**	Sequestrant* mg/1
Jonathan and Delicious apples	20 percent best sugar syrup		
	Tap <sup>a</sup>		
	Distilled		
	Distilled	300	
	Distilled	300	250 CaNa <sub>2</sub> EDTA
	Distilled	300	250 Na-HMP
Montmorency cherries	42.6 g beet sugar per can		
	Tap <sup>a</sup>		
	Distilled		
	Distilled	300	
	Distilled	500	
	Distilled	300	250 CaNa <sub>2</sub> EDTA
	Distilled	300	250 Ca Phytate
	Distilled	300	250 Citric acid
Blue Lake green beans	Commercial Sample <sup>b</sup>	300	250 Na-HMP
	Tap <sup>a</sup>		
	Distilled		
	Distilled	500	
	Distilled	500	300 CaNa <sub>2</sub> EDTA
	Distilled	500	300 Na-HMP
	Distilled	500	300 Ascorbic acid
Commercial Sample <sup>b</sup>			

\*All calculations were based on net fluid content per can.

\*\*Equal amounts of CaCl<sub>2</sub> and MgSO<sub>4</sub> were used to make total mg/1 salts. References in this thesis to "hard water" refer to these minerals and concentrations.

<sup>a</sup>Logan City water contains 46 mg/1 calcium, 19 mg/1 magnesium, 223 mg/1 bicarbonate, 10 mg/1 sulfate, 10 mg/1 chloride, 205 mg/1 total dissolved solids, 192 mg/1 total hardness as calcium carbonate, 185 mg/1 alkalinity, .2 mg/1 chlorine residual and had a pH of 8 (Stephens, 1971).

<sup>b</sup>Commercial samples were purchased in a local supermarket. Cherries were water-packed in Utah and green beans were processed with salt added by the same corporation that provided beans for the experimental work.

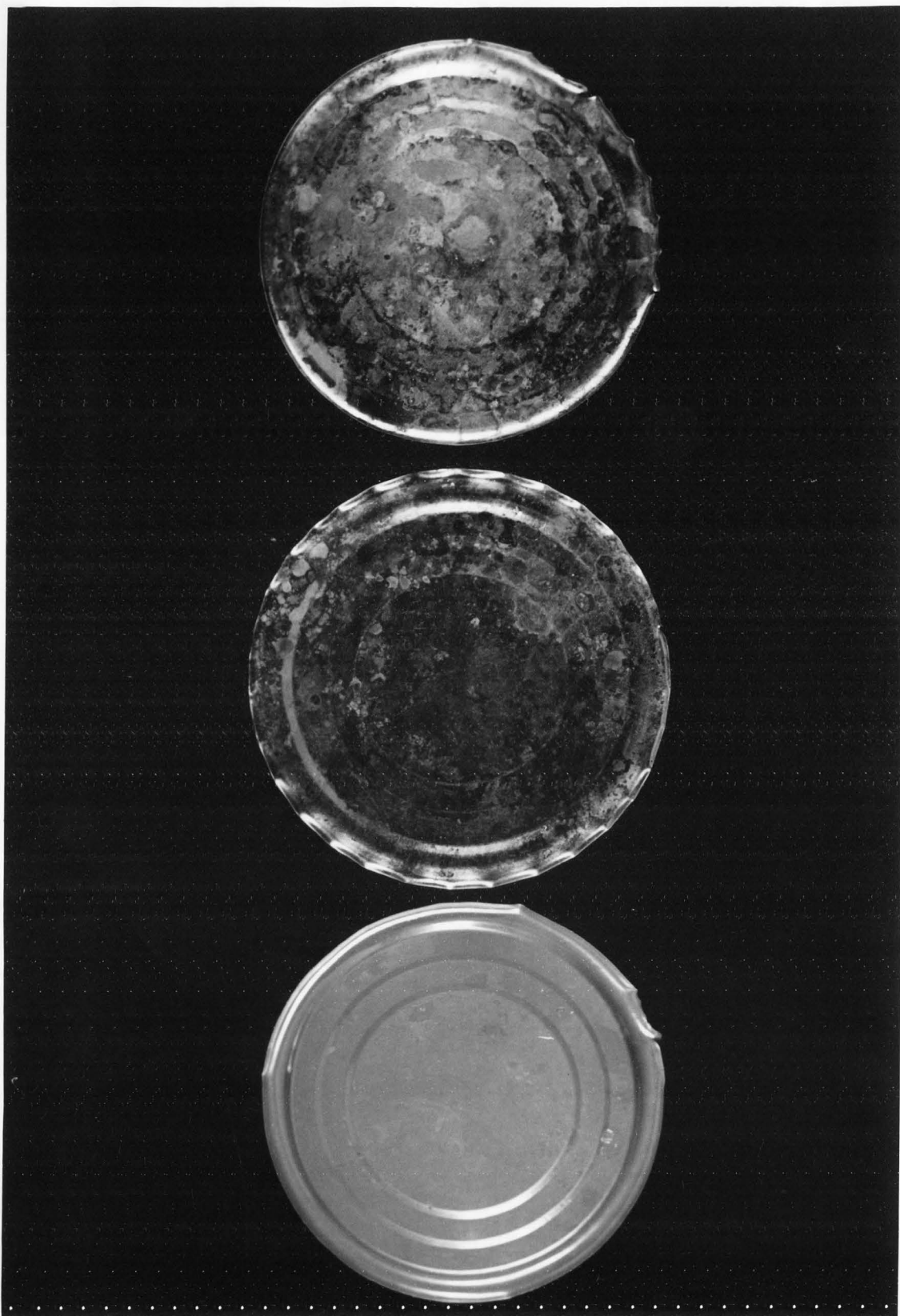


Figure 1. Corrosion of can lids used to process Jonathan apple slices (top to bottom): moderate corrosion of plain tin lid; excessive corrosion of plain tin lid; and no corrosion of C-enamel lid.

### Cherries

Pitted Montmorency cherries, Prunus cerasus, were purchased from Perry Canning Company, Perry, Utah. Preliminary work showed best container fill was obtained using 450 g pitted fruit and 300 ml syrup per 2 1/2 R-enamel can. Vacuum exhaust at 17 lbs pressure was preferable to hot water exhaust and these procedures were used in the main experimental processing. Water variables are shown in Table 1.

Cherries were stored at 35, 75 and 100 F until analysis after 1, 3 and 5 months respectively. Controls of commercially canned sour cherries purchased at a local supermarket were stored with the second and third groups.

### Green beans

Number 4 sieve (medium size) green beans, Phaseolus vulgaris L., (cultivar: Blue Lake), 1 1/2 inch cuts, were received from Del Monte Corporation, Franklin, Idaho. They were transported immediately to the Utah State University processing plant, blanched in 190 F water for 2.5 minutes and cooled in ice water for 2.5 minutes or until cold. Weighed 450 g samples of cooled beans were placed into each 2 1/2 F-enamel can and 450 ml water with one of the variables in Table 1 was added.

Cans were exhausted and sealed with a vacuum of 22 lbs and were processed under 10 lbs pressure (240 F) for 21 minutes in a Master Retort 100. Cans were cooled to below 100 F in cold running water, allowed to dry and stored at room temperature until analyzed 4 months later.

## Physical Analyses

### Shear values

An automatic shear press, Bridge Food Machine Company, Philadelphia, measured the pounds of pressure per square inch required to shear 50 g samples of canned product (Salunkhe et al., 1959).

### Turbidity, percent light transmittance

Diluted samples of product liquor were measured with a Bausch and Lomb 340 spectrophotometer at a range of maximum sensitivity for that product (500 m $\mu$  for cherries; 600 m $\mu$  for apples and beans). Percent transmittance was recorded; distilled water blanks were utilized for standardization.

### Hunter color values

A Hunter Color and Color-Difference Meter, Henry A. Gardner Laboratory, Incorporated, Bethesda, Maryland, was employed to ascertain differences in color due to water treatment and storage. The instrument was standardized with official plates from the National Cannery Association. A red tile with an L (lightness) of 26.5, +a (redness) of 26.9 and +b (yellowness) of 12.9 was utilized for cherry analysis. A white tile of Rd (reflectance) of 86.0, -a (greenness) of 0.6 and +b (yellowness) of 1.2 was used for apple and green bean standardization.

### Internal can corrosion

Corrosion was measured by comparing internal can surfaces to samples shown in Figure 2. A five-point scale (5 = little or no corrosion, 1 = complete detinning of surface in contact with food) was employed.



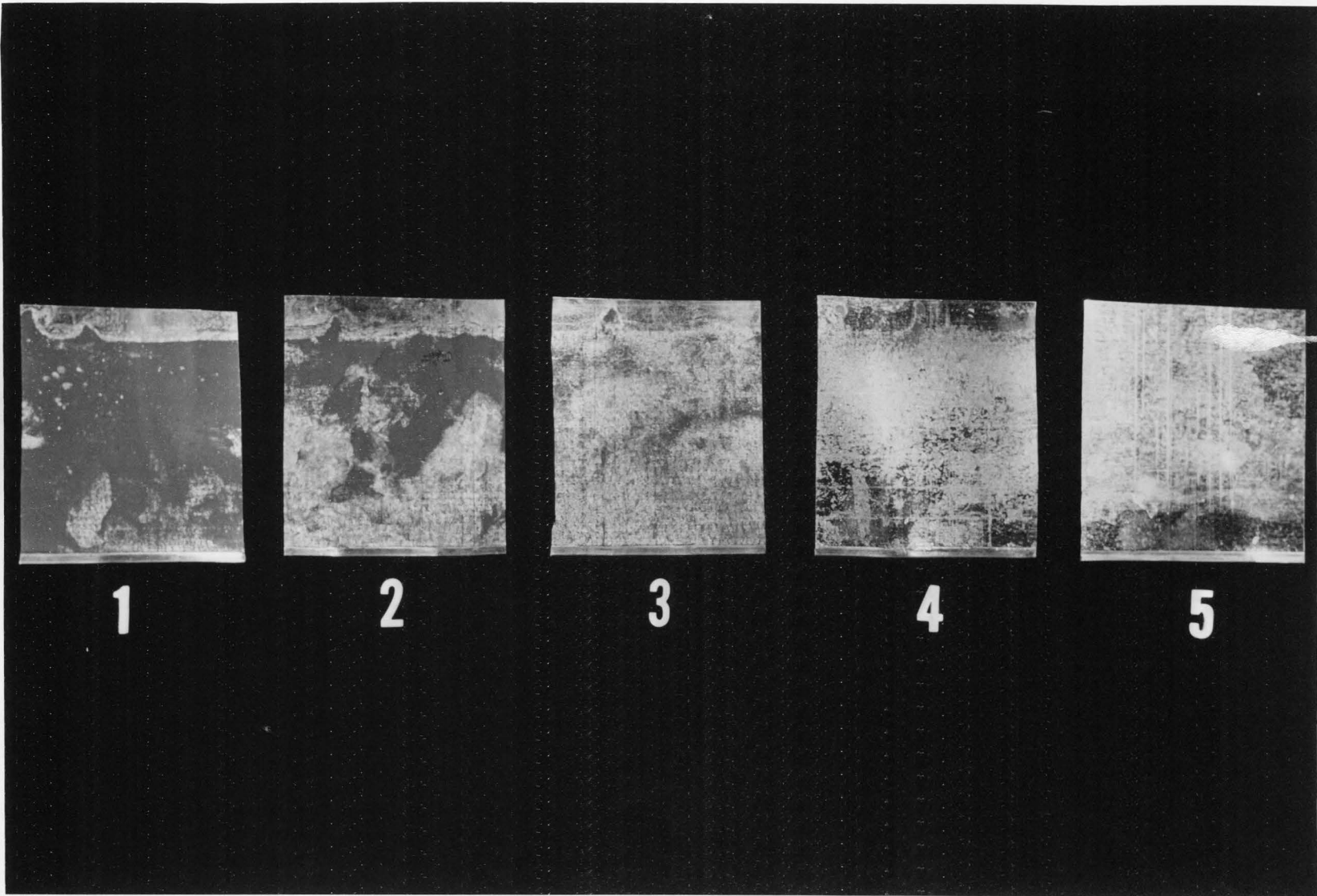


Figure 2. Corrosion standards for evaluation of internal surface detinning of cans used to process Jonathan and Delicious apples.



## Chemical Analyses

### Pectin as calcium pectate

Pectin as calcium pectate present was determined according to the method of Ruck (1969). Fifty g samples were blended with 50 ml of distilled water for 0.5 minutes. An additional 350 ml of water was added to each sample and solutions were boiled for 1 hour, transferred to 500 ml volumetric flasks, cooled and made to volume. After filtering, duplicate 100 ml aliquots were pipetted into flasks and 300 ml of water and 10 ml of 1 N sodium hydroxide added. After 16 hours, 50 ml of 1 N acetic acid, and after 5 additional minutes, 25 ml of 1 N calcium chloride, were added. Samples stood 1 hour, were heated to boiling, boiled 1 minute, filtered and washed on previously weighed hardened, ashless filter papers, placed in covered aluminum weighing dishes, dried overnight at 100 C, cooled in a desiccator for 30 minutes and weighed.

### Volatile reducing substances

*not true*  
The amount of volatile reducing substances (VRS) was determined by steam distilling a mixture of 50 g fruit that had been blended with 50 ml distilled water for 0.5 minutes. According to the method of Luh (1961), the distillate was collected directly in 10 ml of 0.1 N potassium permanganate in 1 N sodium hydroxide. Distillation was continued until about 100 ml of distillate had been collected. After samples were held in darkness for 30 minutes, 10 ml of 5 N sulfuric acid and 10 ml of 30 percent potassium iodide were added and the iodine

liberated was titrated with 0.1 N sodium thiosulfate, using 1 percent soluble starch as indicator. A blank of 100 ml of distilled water was run. Results were reported as microequivalents of potassium permanganate oxidized per 50 g sample.

#### Nitrate-nitrogen

The alpha-naphthylamine method of Hanway and workers (1963) was employed to evaluate nitrate content. One ml of juice was mixed with 20 ml of hot water. After cooling and making to 25 ml volume, duplicate 1 ml samples were removed. Nine ml of 20 percent acetic acid with 0.2 mg/1 copper and 0.4 g of alpha-naphthylamine reagent were added. The mixture was shaken for 10 seconds after 0, 3 and 6 minutes, the samples centrifuged at 10,000 rpm for 3 minutes, filtered and color read as absorbance at 520 m $\mu$  in a Bausch and Lomb 340 spectrophotometer and compared to a standard nitrate curve. Values were reported as ppm nitrate-nitrogen. One ppm nitrate nitrogen = 4.4 ppm nitrate = 7.2 ppm potassium nitrate = 3.3 ppm nitrite = 6.1 ppm sodium nitrate. These values can be used to compare various research work since no consistent method of reporting is found.

#### Total acidity

Total acidity was measured according to the method of Ruck (1969). Fifty g samples and 50 ml of distilled water were blended for 0.5 minutes on a Waring blender. Duplicate 10 ml samples were pipetted into 250 ml beakers and approximately 150 ml of distilled water added. Solutions were titrated to a pH 8.1 endpoint using previously standardized 0.1 N sodium hydroxide and

a Beckman pH meter. Calculations were based on percent malic acid for cherries and apples and on percent citric acid for green beans.

#### Flavinoid pigments

Apple pigments were measured by filtering apple syrup until optically clear and measuring percent transmittance at 600 m $\mu$  with a Bausch and Lomb 340 spectrophotometer. A distilled water blank was used.

#### Anthocyanin pigments

Cherry anthocyanin pigments were measured by the method of Sondheimer and Kertesz (1948). Eighty g samples were blended for 0.5 minutes with 100 ml of Sorenson's citrate buffer (pH 3.4). Solutions were filtered until optically clear and absorbance readings measured with a Bausch and Lomb 340 spectrophotometer at 500 m $\mu$  on solutions of pH 3.4 and 2.0 which had been allowed to develop full red color. The difference was compared to a Congo red standard and multiplied by 1.2 to obtain total anthocyanin values, expressed as mg percent.

#### Organoleptic Evaluation

Selected panels of ten men and women, all non-smokers, evaluated appearance and palatability factors of product and syrup on nine-point scales. Flavor, aroma, texture, color value and fruit shape as well as color value and turbidity of syrup or brine were evaluated in individual booths in a neutral colored room. Palatability was evaluated under colored light to mask color

judgments. Samples were appraised at midmorning and midafternoon. Sample score sheets are shown in Figures 9 to 14.

### Statistical Analyses

Analyses of variance, Duncan's multiple mean comparison range test and correlation coefficients were determined for apple, cherry and green bean data (Ostle, 1963; Duncan, 1955; Steel and Torrie, 1960). A 3 x 2 x 6 factorial analysis was employed for apple data, a 2 x 8 , for cherry work and one-way analysis of variance, for green bean data. The third storage group planned for cherries (100 F for 5 months) was not included in statistical analyses because no water variable possessed acceptable commercial quality at that time; samples purchased at a local market and analyzed with room-temperature stored experimental cherries were not included because no samples could be matched with them in the first (35 F for 1 month) storage group. Duncan's test was not used for apple data because of large significant F values for interactions in analyses of variance for those data.

## RESULTS

Effects of Cultivar, Temperature and Duration of Storage and  
Water Quality on Physical Characteristics of  
Canned Apple Slices

Shear values

Canned Delicious apple slices were significantly more firm than canned Jonathan samples as measured by shear values. Delicious apple slices processed in tap and hard (300 mg/1 salts) water and with added  $\text{CaNa}_2\text{EDTA}$  were firmest for all storage groups. This trend was observed for Jonathan apple slices stored 1 month at 35 F. All Jonathan samples were unacceptably soft when stored at 100 F. Shear values decreased for both cultivars and all water qualities with increasing storage time and temperature from 1 month at 35 F, through 3 months at 75 F to 4 months at 100 F. Addition of 250 mg/1  $\text{CaNa}_2\text{EDTA}$  protected Delicious apple slices against softening during storage at 100 F, but was ineffective for Jonathan samples. Delicious apple slices processed in distilled water and hard water with 250 mg/1 citric acid had lowest shear value determinations when stored at 100 F (Tables 2 and 3).

Turbidity, percent light transmittance

Syrup from canned Jonathan apple slices generally allowed greater light transmittance than did syrup from Delicious apple slices, although results were

Table 2. Effects of water quality, temperature and duration of storage on physical, chemical and organoleptic characteristics of canned Delicious apple slices

Water Quality <sup>a</sup>	Storage: Months per	Temperature F	Physical Characteristics						Chemical		
			Shear Values lb/sq in/50 g	Turbidity, %	Light Transmittance	Hunter Color Values			Corrosion <sup>b</sup>	Calcium Pectate g/50 g	VRS µeg/50 g
						Reflectance (Rd)	Redness (a)	Yellowness (b)			
Tap	1	35	153	65	42.4	11.8	24.6	5.0	.087	128	
	3	75	127	59	41.8	-0.4	18.8	4.2	.067	126	
	4	100	42	35	35.4	5.6	14.8	2.5	.057	143	
Distilled	1	35	110	83	38.6	5.3	21.4	4.1	.081	138	
	3	75	87	73	40.3	3.3	18.0	3.5	.079	123	
	4	100	18	51	34.6	4.6	14.5	2.5	.051	119	
300 mg/1 salts	1	35	165	66	39.6	6.0	22.4	4.3	.068	114	
	3	75	110	64	40.4	3.2	18.2	3.7	.061	126	
	4	100	37	50	32.9	5.9	13.8	2.5	.057	124	
CaNa <sub>2</sub> EDTA	1	35	143	66	42.0	3.8	22.2	3.5	.035	132	
	3	75	123	68	45.3	1.6	18.6	3.2	.063	136	
	4	100	67	52	41.9	3.6	18.1	1.2	.060	185	
Na-HMP	1	35	93	66	41.6	0.6	21.5	4.3	.051	107	
	3	75	77	66	41.0	1.4	16.7	3.7	.058	119	
	4	100	35	39	31.4	6.4	12.5	2.5	.048	197	
Citric Acid	1	35	118	69	41.7	5.2	22.0	4.1	.049	108	
	3	75	93	56	39.0	2.4	15.9	3.5	.050	129	
	4	100	15	33	34.1	5.9	13.6	2.0	.050	202	
F Values from Analyses of Variance											
Cultivars			2316**	47**	248**	68**	38**	235**	236**	101**	
Water			83**	343**	32**	43**	47**	7**	74**	21**	
Storage			2234**	632**	1869**	958**	3569**	363**	115**	558**	
C x W			70**	206**	59**	20**	41**	28**	22**	14**	
C x S			161**	384**	200**	130**	9**	9**	42**	27**	
W x S			18**	100**	6**	30**	21**	5**	23**	39**	
C x W x S			9**	98**	27**	33**	16**	6**	19**	13**	

<sup>a</sup>See Table 1 for explanation of water qualities.

<sup>b</sup>Subjective evaluation: 5 = no detinning, 1 = completely detinned.

<sup>c</sup>Subjective evaluation: 9 = extremely firm; 5 = optimum texture; 1 = completely mushy and disintegrating.

<sup>d</sup>Subjective evaluation: 9 = completely acceptable, 1 = completely unacceptable.

Characteristics			Organoleptic Characteristics							
Nitrate-Nitrogen mg/l	Acidity, as % Malic Acid	Pigment, % Light Transmittance	Firmness <sup>c</sup>	Fruit Shape <sup>d</sup>	Turbidity <sup>d</sup>	Flavor <sup>d</sup>	Aroma <sup>d</sup>	Fruit Color <sup>d</sup>	Color Uniformity <sup>d</sup>	Syrup Color <sup>d</sup>
9.8	.079	93	6.6	7.3	4.3	6.5	6.1	4.0	7.8	5.4
4.9	.091	95	6.7	7.6	5.7	7.1	6.7	6.9	7.8	6.5
2.7	.114	87	5.1	7.0	4.6	5.7	5.9	5.7	5.1	4.8
9.9	.073	95	5.5	6.9	6.6	6.5	6.7	4.3	5.0	7.2
5.3	.070	94	5.4	7.3	6.3	5.9	6.9	5.8	5.8	6.2
3.8	.097	86	3.4	6.1	5.0	4.8	5.0	4.2	6.0	5.0
9.5	.077	95	6.4	6.9	5.2	5.4	6.6	2.7	5.7	5.7
4.5	.075	94	6.1	7.3	5.3	6.3	7.0	3.8	5.0	6.4
5.5	.094	86	3.8	7.0	4.5	4.8	5.8	3.3	5.5	4.8
9.9	.085	93	7.0	7.4	6.3	6.0	6.5	5.8	5.5	7.1
3.6	.070	98	6.2	7.6	6.2	6.6	7.4	5.7	5.7	6.5
5.8	.105	90	5.9	7.6	6.8	6.8	6.4	7.5	6.7	7.6
9.8	.096	94	6.0	7.6	5.5	6.1	6.3	6.7	7.0	6.4
4.1	.099	93	5.1	7.5	5.6	6.2	5.8	7.0	6.7	6.6
4.8	.127	78	2.9	6.5	5.0	4.6	5.2	3.3	5.7	4.8
9.6	.079	93	6.2	7.6	6.0	6.5	6.0	7.3	7.0	7.2
4.4	.092	96	5.9	7.4	5.2	6.2	6.6	7.4	6.6	6.3
3.4	.124	73	3.2	6.5	4.1	4.6	5.1	4.5	6.4	4.0
768**	30390**	3015**	1910**	75**	246**	77**	399**	281**	11**	95**
20**	16**	410**	66**	24**	27**	11**	16**	45**	52**	18**
1682**	448**	4425**	652**	303**	305**	876**	397**	396**	91**	618**
14**	37**	130**	22**	8**	25**	14**	19**	51**	9**	36**
63**	28**	497**	8**	105**	75**	245**	19**	144**	61**	66**
15**	10**	147**	4**	11**	22**	9**	7**	33**	7**	28**
24**	5**	233**	12**	7**	17**	10**	12**	23**	15**	31**

\*\*Significance at .01 level.

Table 3. Effects of water quality, temperature and duration of storage on physical, chemical and organoleptic characteristics of canned Jonathan apple slices

Water Quality <sup>a</sup>	Storage: Months per	Temperature F	Physical Characteristics						Chemical	
			Shear Values lb/sq in/50 g	Turbidity, % Light Transmittance	Hunter Color Values			Corrosion <sup>b</sup>	Calcium Pectate g/50 g	VRS $\mu$ eq/50 g
					Reflectance (Rd)	Redness (a)	Yellowness (b)			
Tap	1	35	75	61	45.5	1.6	22.7	3.0	.073	118
	3	75	58	63	44.1	0.8	17.6	2.7	.053	131
	4	100	12	53	35.3	5.4	15.0	2.2	.056	183
Distilled	1	35	60	69	50.0	0.1	22.2	2.8	.062	169
	3	75	48	64	42.8	0.8	17.2	2.7	.035	129
	4	100	67	54	33.2	8.5	13.7	1.8	.045	180
300 mg/1 salts	1	35	71	59	45.5	2.4	20.6	2.5	.059	122
	3	75	52	59	43.1	2.0	16.6	2.3	.045	136
	4	100	10	52	36.3	4.0	15.4	1.5	.044	177
CaNa <sub>2</sub> EDTA	1	35	77	70	47.2	2.2	21.4	4.5	.051	118
	3	75	47	65	42.7	0.4	16.1	3.6	.044	143
	4	100	8	45	31.3	5.5	14.4	1.5	.038	223
Na-HMP	1	35	63	74	47.3	0.9	22.0	3.3	.058	121
	3	75	57	64	43.5	0.6	17.1	2.5	.052	133
	4	100	26	46	34.9	6.4	14.7	1.7	.039	190
Citric Acid	1	35	64	70	45.9	1.5	22.8	3.0	.054	118
	3	75	47	57	43.4	-.1	16.2	2.2	.048	129
	4	100	18	54	33.0	9.4	13.4	1.7	.038	183

<sup>a</sup>See Table 1 for explanation of water qualities.

<sup>b</sup>Subjective evaluation: 5=no detinning, 1=completely detinned.

<sup>c</sup>Subjective evaluation: 9 = extremely firm, 5 = optimum texture, 1 = completely mushy and disintegrating.

<sup>d</sup>Subjective evaluation: 9 = completely acceptable, 1 = completely unacceptable.



Characteristics			Organoleptic Characteristics							
Nitrate-Nitrogen mg/l	Acidity, as % Malic Acid	Pigment, % Light Transmittance	Firmness <sup>c</sup>	Fruit Shape <sup>d</sup>	Turbidity <sup>d</sup>	Flavor <sup>d</sup>	Aroma <sup>d</sup>	Fruit Color <sup>d</sup>	Color Uniformity <sup>d</sup>	Syrup Color <sup>d</sup>
5.2	.224	91	4.5	7.2	6.4	6.4	5.7	7.2	7.2	7.5
2.3	.257	90	4.5	7.9	6.4	6.8	6.0	7.4	7.0	7.2
1.6	.270	88	2.1	6.4	6.7	3.6	5.2	5.7	6.7	6.9
4.2	.256	90	3.6	7.6	7.6	6.5	5.7	7.8	7.5	7.4
4.2	.265	90	3.3	6.5	7.0	6.6	6.0	7.4	6.2	7.6
1.9	.281	86	2.0	3.7	4.2	3.1	4.5	3.8	5.2	4.4
7.1	.234	88	3.6	6.9	6.2	6.6	6.0	6.9	6.2	6.4
3.9	.264	87	3.4	7.6	6.7	6.2	5.9	6.9	5.9	7.0
1.7	.275	84	2.1	5.9	5.1	3.9	4.6	5.7	6.1	5.7
7.9	.239	89	4.5	7.4	7.6	6.7	5.9	7.8	7.1	7.9
3.4	.238	90	4.1	7.6	7.1	6.6	6.2	7.8	7.1	7.4
1.6	.284	75	2.2	4.7	4.4	2.8	3.3	3.0	4.2	3.8
8.8	.232	89	4.1	7.9	7.3	7.0	5.8	8.2	7.6	7.8
3.3	.255	88	3.5	7.8	6.6	6.9	6.2	7.8	7.4	7.0
2.3	.283	80	2.6	5.7	4.5	3.0	4.6	4.6	5.5	3.9
6.8	.241	86	3.4	7.3	7.1	6.9	5.8	7.7	7.4	7.6
3.6	.258	80	3.4	7.7	7.2	6.1	5.4	8.1	7.6	7.6
3.5	.269	80	2.0	4.7	4.7	2.8	3.9	3.1	5.1	4.1

not consistent among water treatments or storage variables. Turbidity increased significantly for all water treatments of both cultivars when storage duration and temperature increased from 1 month at 35 F to 4 months at 100 F. Turbidity values were lower for syrup from Jonathan apple slices stored 1 month at 35 F and processed in distilled water or water with 250 mg/l  $\text{CaNa}_2\text{EDTA}$ , Na-HMP or citric acid than for similar samples processed in tap or hard waters. Syrup from Delicious apple slices processed in distilled water and stored 1 month at 35 F was significantly less turbid than syrup from all other samples. Turbidity increased with increased storage. It was greatest in syrup from Delicious apple slices processed in tap water or water with added Na-HMP and citric acid and syrup from Jonathan slices processed in water with added  $\text{CaNa}_2\text{EDTA}$  and Na-HMP (Tables 2 and 3).

#### Hunter color values

Canned Jonathan apple slices had significantly higher reflectance and lower redness values than canned Delicious apple slices when stored 1 month at 35 F and measured with a Hunter Color and Color Difference Meter. Jonathan samples processed in tap and hard waters were less yellow and other water treatments more yellow than corresponding Delicious samples when stored 1 month at 35 F. For samples of both cultivars, reflectance decreased as storage increased from 1 month at 35 F to 3 months at 75 F to 4 months at 100 F; redness decreased from 1 month at 35 F to 3 months at 75 F, but increased markedly after 4 month storage at 100 F. Degree of yellowness decreased as storage increased for both cultivars. Addition of 250 mg/l

CaNa<sub>2</sub>EDTA to canned Delicious apple slices protected them from color deterioration as evidenced by high reflectance and low redness scores (Tables 2 and 3).

### Corrosion

Cans containing Jonathan apple slices exhibited more internal can corrosion than those with Delicious apple slices, except for cans with added CaNa<sub>2</sub>EDTA; for these cans the reverse was noted. Corrosion increased with increasing storage time and temperature for all water treatments of both cultivars. All cans were severely detinned when stored 4 months at 100 F, although the least damage was noted for Delicious apple slices canned in tap, distilled or hard water or those with 250 mg/l Na-HMP and for Jonathan apple slices canned in tap water. When stored at 35 F for 1 month or 75 F for 3 months, cans from Jonathan apple slices with 250 mg/l CaNa<sub>2</sub>EDTA showed less corrosion than other water treatments. Cans with Delicious apple slices and CaNa<sub>2</sub>EDTA showed the most corrosion of all Delicious samples at all three storage durations and temperatures (Tables 2 and 3).

The present study showed water impurities also increased corrosion. Copper chloride began corroding unenameled cans as soon as contact was made with the metal surface. Corrosion was extensive when Jonathan apples were packed with ferric sulfate in unenameled cans. It was observed that apple color was better for samples containing copper chloride if unenameled rather than enameled cans were used (Figures 3 and 4). It appeared that if copper

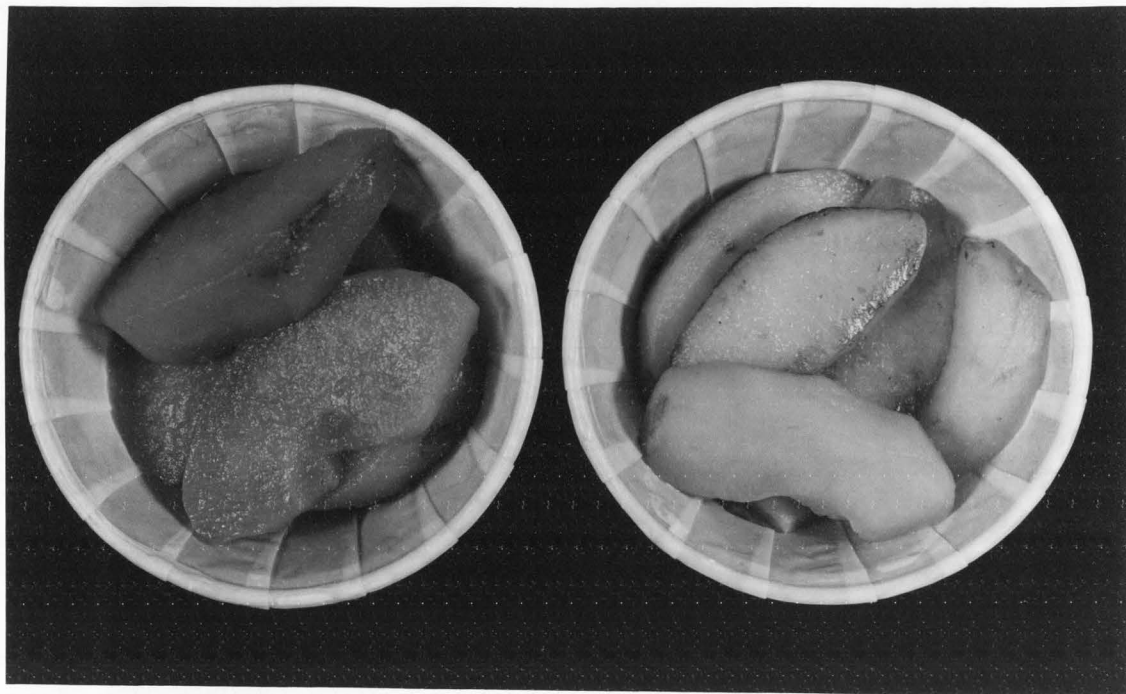


Figure 3. Discoloration of Jonathan apple slices canned in C-enamel coated and plain tin containers when processed with water containing 1000 mg/l copper chloride.

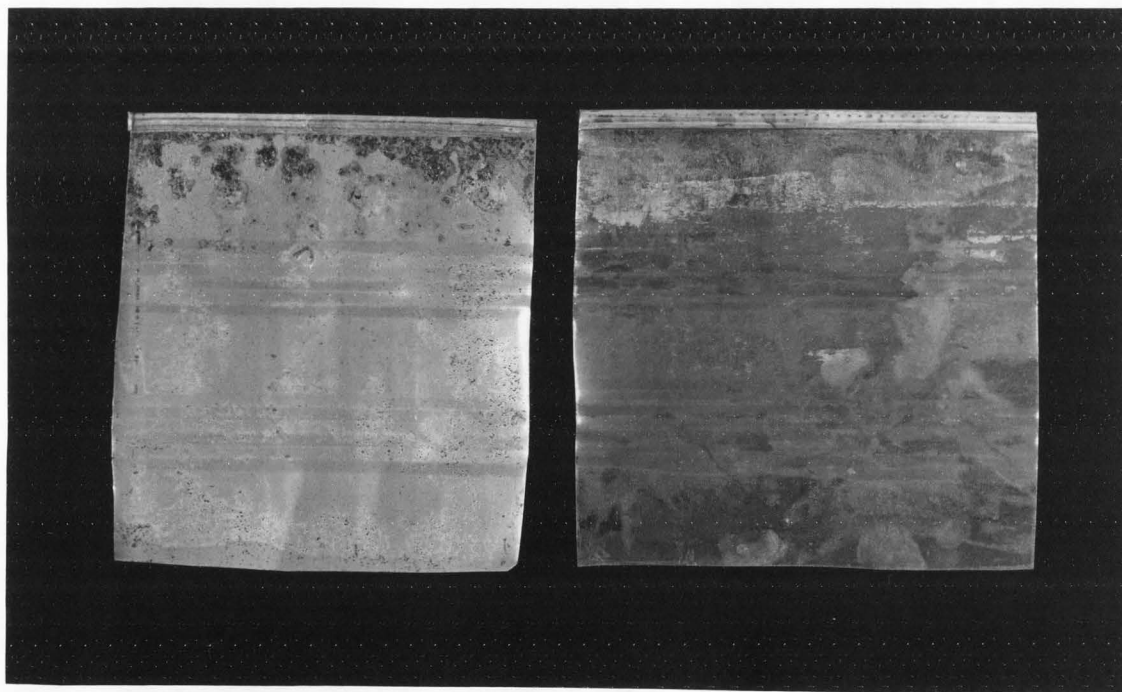


Figure 4. Detinning of C-enamel coated and plain tin cans containing Jonathan apple slices and water with 1000 mg/l copper chloride.

chloride were free to react with the can's metal surface it caused less severe reaction with the apple itself.

Effects of Cultivar, Temperature and Duration of Storage and  
Water Quality on Chemical Characteristics of  
Canned Apple Slices

Pectin as calcium pectate

Calcium pectate values were greater for Delicious apple slices than for Jonathan apple slices when processed in tap, hard and distilled waters and for those processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$ , Na-HMP and citric acid when stored 3 months at 75 F or 4 months at 100 F. Calcium pectate values decreased with increasing storage temperature and duration, except for Delicious apple slices canned with  $\text{CaNa}_2\text{EDTA}$  which increased with increasing storage and for Delicious apple slices treated with citric acid which did not change in calcium pectate content with storage. After 4 month storage at 100 F, samples with highest calcium pectate content included Delicious apple slices processed in tap or hard water and with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  and Jonathan samples processed in tap water. All samples with added sequestrants had lower calcium pectate values than non-chelated samples except for Delicious samples treated with  $\text{CaNa}_2\text{EDTA}$  (Tables 2 and 3).

Volatile reducing substances

Canned Jonathan apple slices had significantly more volatile reducing substances than did canned Delicious samples and values increased as storage time and temperature increased. Canned Jonathan samples with 250 mg/1

CaNa<sub>2</sub>EDTA had the highest VRS content when stored at 75 and 100 F for 3 and 4 months, respectively (Tables 2 and 3).

#### Nitrate-nitrogen

Canned Delicious apple slices had higher nitrate-nitrogen content than did canned Jonathan apple samples. Nitrate-nitrogen values decreased with increasing time and temperature, except for Delicious samples processed in hard water or with 250 mg/1 CaNa<sub>2</sub>EDTA or Na-HMP which decreased from 1 month at 35 F to 3 months at 75 F but increased again upon storage for 4 months at 100 F. Few differences due to water quality were noted for Delicious apple slices except when stored at 100 F, at which time samples processed with hard water and 250 mg/1 CaNa<sub>2</sub>EDTA had higher values than other treatments. Canned Jonathan apple slices processed in hard water or with 250 mg/1 Na-HMP or CaNa<sub>2</sub>EDTA had higher values when stored 1 month at 35 F than other samples. After 4 months storage at 100 F citric acid treated Jonathan apple slices had the highest nitrate-nitrogen values of any treatments (Tables 2 and 3).

#### Total acidity

Canned Jonathan apple slices were significantly greater in total acid than canned Delicious samples. Total acidity increased with increasing storage, 1, 3 and 4 months at 35, 75 and 100 F, respectively. Few differences were noted among water qualities (Tables 2 and 3).

### Pigment

Syrup from canned Delicious apple slices had less pigment than syrup from canned Jonathan slices when stored 1 and 3 months at 35 and 75 F, respectively. Pigment became darker with increased storage. Addition of 250 mg/1 CaNa<sub>2</sub>EDTA to Delicious apple syrup prevented pigment degradation (Tables 2 and 3).

### Effects of Cultivar, Temperature and Duration of Storage and Water Quality on Organoleptic Characteristics of Canned Apple Slices

### Firmness

Canned Delicious apple slices were significantly more firm than canned Jonathan apple slices but firmness of both cultivars decreased significantly as storage duration and temperature increased from 1 or 3 months at 35 and 75 F, respectively, to 4 months at 100 F. Samples processed in tap water and with 250 mg/1 CaNa<sub>2</sub>EDTA were the most firm for both cultivars and in all storage groups, except that no treatment retained firmness of Jonathan samples stored 4 months at 100 F. Delicious apple slices were least firm when processed in distilled water and Jonathan samples, least firm in distilled water or with 250 mg/1 citric acid (Tables 2 and 3).

### Fruit shape

All canned apple slices retained acceptable shape throughout the study except for Jonathan apple slices processed in distilled water and stored 4 months



at 100 F. Best shape retention upon 100 F storage was noted for Delicious apple slices processed in tap and hard water or with 250 mg/l  $\text{CaNa}_2\text{EDTA}$  (Tables 2 and 3).

#### Syrup turbidity

Syrup from canned Jonathan apple slices was significantly less turbid than syrup from canned Delicious samples. No significant differences were found among syrups stored 1 or 3 months at 35 and 75 F respectively; however syrup became significantly more turbid when stored 4 months at 100 F. Only Delicious apple syrup with 250 mg/l  $\text{CaNa}_2\text{EDTA}$  and tap water syrup from Jonathan apple slices retained acceptable turbidity scores at that time. Syrup of both cultivars and all water qualities except tap water syrup from Delicious samples were of acceptable quality when stored 1 and 3 months at 35 and 75 F, respectively (Tables 2 and 3).

#### Flavor

The flavor of one cultivar was not consistently preferred over the flavor of the other and none were objectionable in flavor except for Jonathan apple slices stored 4 months at 100 F. At this temperature no water treatment was effective in maintaining Jonathan apple flavor (Tables 2 and 3). Some judges detected a "tin" or "metallic" taste and odor in apples, particularly Jonathan samples. The comment was most prevalent with samples from detinned cans and was made for samples from all three storage groups.



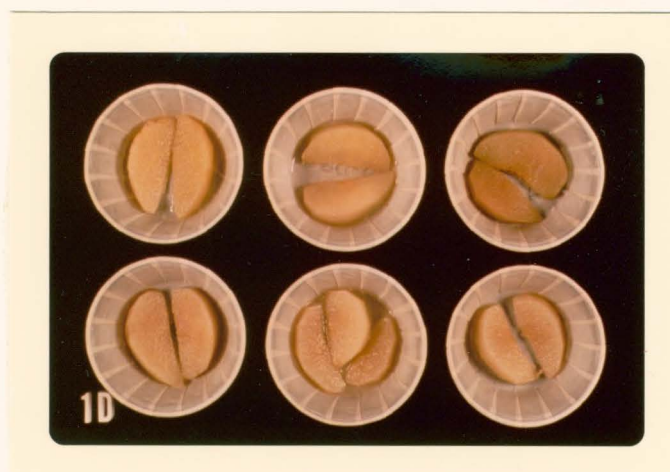
### Aroma

Aroma of canned Delicious apple slices was preferred to that of Jonathan samples, being described as "sweeter" and "more like fresh apple." No samples were objectionable in aroma except Jonathan slices stored 4 months at 100 F. Aroma scores for other cultivars tended to increase as storage duration and temperature increased from 1 to 3 months at 35 and 75 F, respectively, then decreased significantly when stored 4 months at 100 F. Addition of 250 mg/1 CaNa<sub>2</sub>EDTA to Delicious apple slices before processing prevented aroma degradation upon storage at 100 F (Tables 2 and 3).

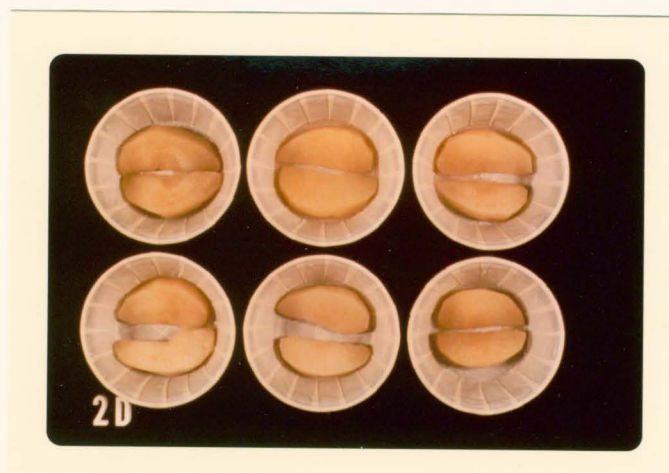
### Fruit color value

Canned Jonathan apple slices received significantly higher fruit color scores by panels of judges than canned Delicious samples when stored 1 month at 35 F. Delicious apple slices improved in color when stored 3 months at 75 F but still were less acceptable than Jonathan samples. All samples except Delicious apple slices with 250 mg/1 CaNa<sub>2</sub>EDTA deteriorated significantly after 4 month storage at 100 F. At that time all samples were rated unacceptable except for Delicious apple slices with CaNa<sub>2</sub>EDTA and those processed in tap water and Jonathan samples processed in tap and hard waters (Tables 2 and 3; Figures 5 and 6).

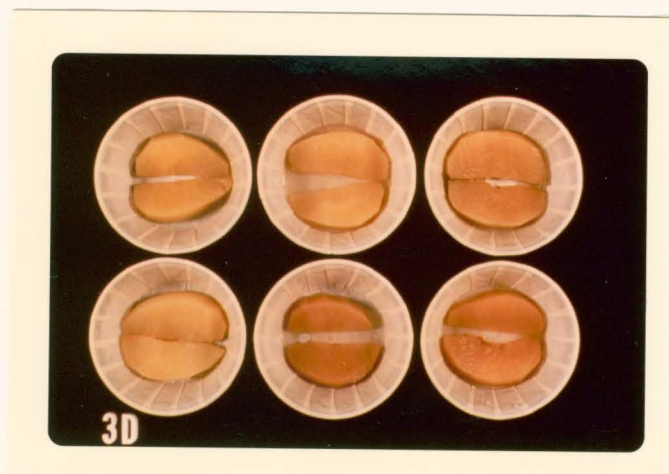
Preliminary investigation in 1969 showed that copper and iron salts added to syrup of canned Jonathan and Delicious apple slices caused extensive discoloration (Figure 7). Copper chloride caused blue discoloration at low levels (10 to 100 mg/1); at higher concentration blue-green color and finally



1 month storage at 35 F

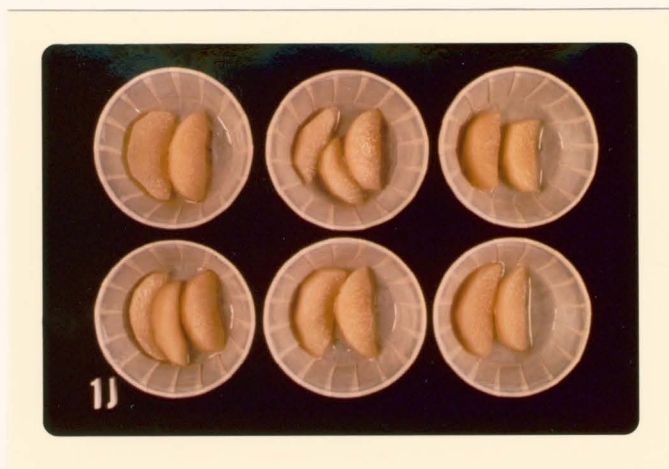


3 month storage at 75 F

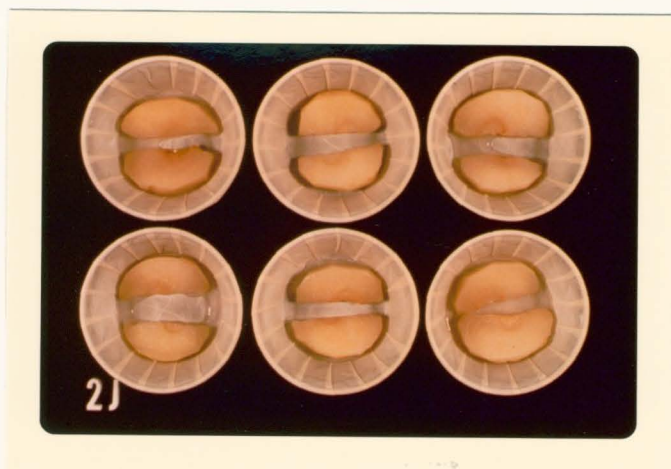


4 month storage at 100 F

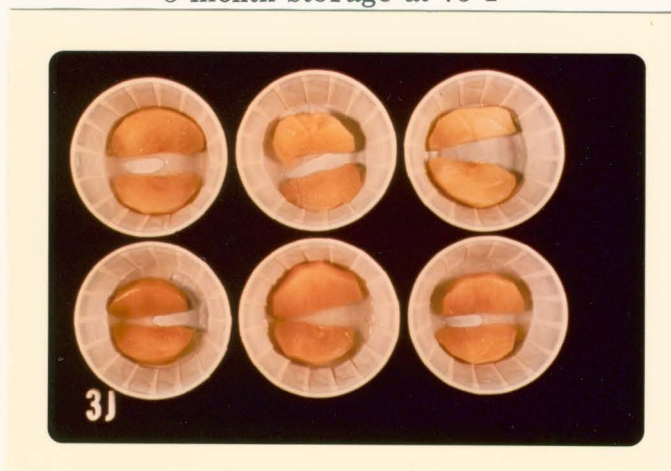
Figure 5. Effects of water quality and temperature and duration of storage on appearance of canned Delicious apple slices. Row 1: tap, distilled and distilled water with 300 mg/l salts processed samples. Row 2:  $\text{CaNa}_2\text{EDTA}$ , Na-HMP and citric acid treated samples.



1 month storage at 35 F



3 month storage at 75 F



4 month storage at 100 F

Figure 6. Effects of water quality and temperature and duration of storage on appearance of canned Jonathan apple slices. Row 1: tap, distilled and distilled water with 300 mg/l salts processed samples. Row 2:  $\text{CaNa}_2\text{EDTA}$ , Na-HMP and citric acid treated samples.

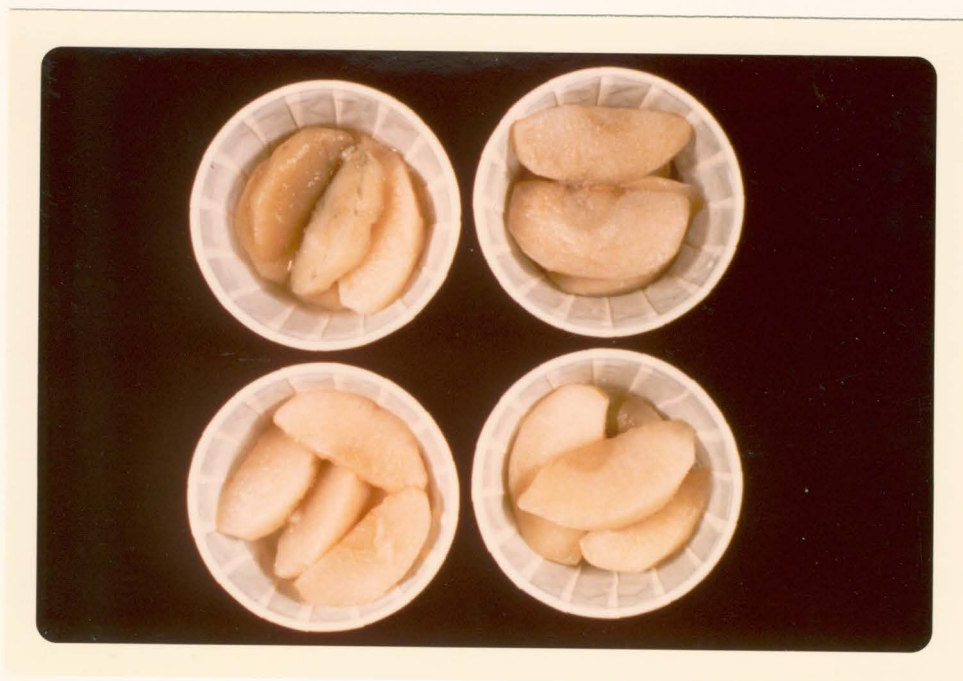


Figure 7. Effects of water quality, temperature and duration of storage on appearance of Jonathan apple slices canned in water containing (top row) ferric sulfate, copper chloride, (bottom row) magnesium sulfate and calcium chloride at the level of 150 mg/l salts content.



blackening of apple slices was observed. Ferric sulfate resulted in dullness and pink casts in apples at all concentrations, particularly in Jonathan apple slices; in them any iron caused unacceptable color. Calcium salts caused increased yellowness and dullness of apples and was especially noticeable in Jonathan samples. Delicious apple color was acceptable but yellow if less than 100 mg/1 calcium chloride was added. Magnesium sulfate also caused yellowing; it was not as detrimental to Jonathan apple slice color as calcium salts were.

#### Color uniformity

Jonathan apple slices were rated significantly higher than canned Delicious samples in color uniformity when stored 1 and 3 months at 35 and 75 F, respectively, except for Delicious samples processed in tap water which received higher uniformity scores than any other samples. Color uniformity values decreased with 4 month storage at 100 F except for Delicious samples with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  and samples of both cultivars processed in hard water. No samples received unacceptable uniformity scores except Jonathan apples with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  stored 4 months at 100 F (Tables 2 and 3).

#### Syrup color value

Syrup from canned Jonathan apples received significantly higher color scores than syrup from canned Delicious apple slices. Syrup color values either were not significantly different or increased as storage increased from 1 month at 35 F to 3 months at 75 F, then decreased significantly upon 4 month

storage at 100 F, except for Delicious apple syrup with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  which continued to improve in color acceptability throughout the study. Delicious apple syrup made with distilled water and Jonathan syrup from tap and hard waters were also acceptable after 4 months at 100 F (Tables 2 and 3).

Effects of Temperature and Duration of Storage and Water Quality  
on Physical Characteristics of Canned Montmorency Cherries

Shear values

Shear values decreased significantly with increasing storage temperature and duration from 1, 3 to 5 months at 35, 75 and 100 F, respectively (Table 4). Shear values were highest for cherries processed in hard (500 mg/1) water followed by those processed in tap water, hard (300 mg/1) water and then by those with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  and calcium phytate. Shear values were significantly higher for the above variables than for those processed in distilled water, commercially, or with 250 mg/1 Na-HMP or citric acid according to results obtained using Duncan's Multiple Mean Comparison Range Test (Table 7).

Turbidity, percent light transmittance

Percent light transmittance through Montmorency cherry syrup as measured with a Bausch and Lomb 340 spectrophotometer was ineffective as a method of measuring turbidity, because the character of the turbid material changed with storage. When cans were stored 1 month at 35 F, the turbidity of the syrup was in the form of very fine particles suspended throughout the syrup. As storage increased to 3 months at 75 F and 5 months at 100 F, the

Table 4. Effects of water quality, temperature and duration of storage on physical, chemical and organoleptic characteristics of canned Montmorency cherries

Water Quality <sup>a</sup>	Storage: Mo. per	Temperature F	Physical Characteristics					Chemical		
			Shear Values lb/sq in/50 g	Turbidity, % Light	Transmittance	Hunter Color Values			Calcium Pec- tate g/50 g	VRS, µeq/50 g
						Lightness (L)	Redness (a)	Yellowness (b)		
Tap	1	35	82.5	20.0	23.1	22.0	9.6	.0087	224.0	
	3	75	71.7	29.0	22.2	19.0	8.9	.0134	187.2	
	5	100	40.0	40.0	16.9	4.6	6.6	.0178		
Distilled	1	35	57.5	24.3	21.8	22.9	9.1	.0056	204.3	
	3	75	57.5	31.5	21.0	19.1	8.2	.0130	177.0	
	5	100	20.0	44.0	18.4	9.7	6.8	.0249		
300 mg/1 salts	1	35	75.0	24.0	21.9	21.6	8.9	.0064	204.3	
	3	75	80.8	29.3	22.0	20.2	8.8	.0126	156.2	
500 mg/1 salts	1	35	97.5	17.5	21.9	21.6	8.9	.0064	204.3	
	3	75	85.0	24.2	22.7	19.6	9.2	.0111	167.7	
	5	100	40.0	46.0						
CaNa <sub>2</sub> EDTA	1	35	74.2	28.2	22.3	24.9	9.4	.0085	202.8	
	3	75	65.0	30.7	23.1	20.4	9.4	.0156	178.0	
	5	100		44.0	19.0	9.1	7.1			
Calcium Phytate	1	35	70.8	23.4	22.3	22.4	9.0	.0120	204.7	
	3	75	59.2	30.8	21.8	21.1	9.5	.0156	178.0	
	5	100	20.0	41.0				.0303		
Na-HMP	1	35	63.3	24.0	22.3	22.4	9.0	.0120	204.7	
	3	75	45.0	31.5	23.1	20.4	9.4	.0107	169.7	
Citric Acid	1	35	59.2	22.8	21.7	21.2	8.7	.0068	182.5	
	3	75	53.3	29.5	22.1	20.4	9.4	.0107	205.3	
	5	100		44.0	18.0	8.7	6.6			
Commercial	3	75	44.2	4.7	24.7	16.2	8.9	.0108	259.2	
F Values (1 and 3 month storage only)										
Water			53.4**	9.1**	6.9**	11.2**	4.1**	5.9**	5.5**	
Storage			39.0**	109.6**	3.1*	175.4**	3.2**	122.5**	60.2**	
W x S			4.7**	1.0	5.8**	10.1**	6.2**	6.6**	6.9**	

<sup>a</sup>See Table 1 for an explanation of water qualities.

<sup>b</sup>Subjective evaluation: 9 = extremely firm, 5 = optimum texture, 1 = completely mushy and disintegrating.

<sup>c</sup>Subjective evaluation: 9 = completely acceptable, 1 = completely unacceptable.





particles coalesced, often precipitated and became more objectionable to the eye. However, because of precipitation of the particles, the percent light transmittance increased with increasing storage, incorrectly indicating less turbidity. Therefore comparisons should be made only among intra-storage groupings. Based upon this restriction, Montmorency cherries processed with 250 mg/1 CaNa<sub>2</sub>EDTA were the least turbid of samples stored 1 month at 35 F. Samples processed in distilled water or with 250 mg/1 Na-HMP were least turbid and commercially processed samples, the most turbid of samples stored at 75 F for 3 months. Tap and hard water syrups were more turbid than distilled water or syrups containing sequestrants (Table 4).

#### Hunter color values

Hunter redness and yellowness values decreased significantly as storage of canned Montmorency cherries increased from 1, 3 to 5 months at 35, 75 and 100 F, respectively. Lightness values decreased when stored 5 months at 100 F, but few consistent differences were noted among samples stored at 35 F for 1 month or 75 F for 3 months (Table 4). Cherries with 250 mg/1 CaNa<sub>2</sub> EDTA ranked highest in lightness, redness and yellowness values. Cherries processed in tap water and hard (500 mg/1) water ranked lowest in redness values and those packed in distilled or hard (300 and 500 mg/1) waters were lowest in yellowness values. Canned cherries with 250 mg/1 CaNa<sub>2</sub>EDTA or Na-HMP were significantly higher in redness than samples packed with water containing 500 mg/1 salts, tap water or 250 mg/1 citric acid and were

significantly higher in yellowness than samples packed in distilled or hard waters according to results of Duncan's tests (Table 7).

Effects of Temperature and Duration of Storage and Water Quality  
on Chemical Characteristics of Canned Montmorency Cherries

Pectin as calcium pectate

Pectin as calcium pectate increased significantly as storage of canned sour cherries increased from 1 month at 35 F to 3 months at 75 F to 5 months at 100 F (Table 4). Duncan's tests showed canned cherries processed with 250 mg/1 calcium phytate or  $\text{CaNa}_2\text{EDTA}$  were significantly higher in calcium pectate than cherries processed with 250 mg/1 citric acid, distilled or hard waters (Table 7).

Volatile reducing substances

Volatile reducing substances (VRS) decreased significantly for canned Montmorency cherries as storage increased from 1 month at 35 F to 3 months at 75 F, except for cherries processed with 250 mg/1 citric acid for which the opposite was true (Table 4). Commercial samples had the highest VRS values, followed by cherries processed in tap water; they were significantly higher than samples with 300 mg/1 salts, 500 mg/1 salts or 250 mg/1 Na-HMP or calcium phytate (Table 7).

Anthocyanin content

Anthocyanin content of canned sour cherries decreased significantly as storage increased from 1 month at 35 F to 3 months at 75 F (Table 4). Canned

sour cherries with 250 mg/1 Na-HMP were significantly higher in anthocyanin than commercial samples, cherries processed in water with 300 or 500 mg/1 salts, 250 mg/1 citric acid or calcium phytate or those processed in distilled water. Canned sour cherries processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  were significantly higher in anthocyanin content than commercial samples or those processed in water with 300 or 500 mg/1 salts or citric acid (Table 7).

#### Total acidity

Total acidity increased with increasing storage of canned Montmorency cherries except for samples processed in tap or distilled water, for which the reverse trend was evident (Table 4). For samples stored at 75 F for 3 months, total acidity values were highest in samples processed with 250 mg/1 Na-HMP, calcium phytate or hard waters. Lowest total acidity values were observed for sour cherries processed in tap water (Table 7).

### Effects of Temperature and Duration of Storage and Water Quality on Organoleptic Characteristics of Canned Montmorency Cherries

#### Firmness

No significant differences in firmness judged subjectively were noted among canned sour cherries stored 1 month at 35 F or 3 months at 75 F except that commercial samples were significantly softer than any experimentally processed cherries (Table 4). Cherries canned in water with 300 mg/1 salts

were significantly more firm than those with 250 mg/1 citric acid, Na-HMP or  $\text{CaNa}_2\text{EDTA}$  or commercial samples (Table 7).

#### Fruit shape

As storage increased from 1, 3 to 5 months at 35, 75 and 100 F, respectively, shape of cherries judged subjectively decreased significantly (Table 4). Cherries with 250 mg/1 citric acid were significantly better in shape than those processed in tap or hard waters. Commercial samples were significantly lower in shape acceptability than any laboratory processed sour cherries (Table 7).

#### Syrup turbidity

Syrup from canned Montmorency cherries became more turbid as storage increased in duration from 1, 3 to 5 months at temperatures of 35, 75 and 100 F, respectively, according to subjective evaluation (Table 4). Syrup with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  possessed most clarity, while syrup from commercial samples was most turbid. Syrup made with hard waters was significantly more turbid than syrups of other experimental water qualities tested. Syrup containing  $\text{CaNa}_2\text{EDTA}$  also was significantly more clear than syrup with 250 mg/1 Na-HMP or syrup with tap water. Distilled water syrups or those with added calcium phytate were significantly clearer than those with Na-HMP (Table 7).

### Flavor

Flavor values of canned Montmorency cherries decreased as storage increased from 1, 3 to 5 months at 35, 75 and 100 F respectively (Table 4). No significant differences in flavor among water qualities were noted, although those samples processed in distilled water ranked highest in flavor and those in hard water ranked lowest of laboratory-processed cherries. Commercial samples were lower in flavor than other canned cherries.

### Aroma

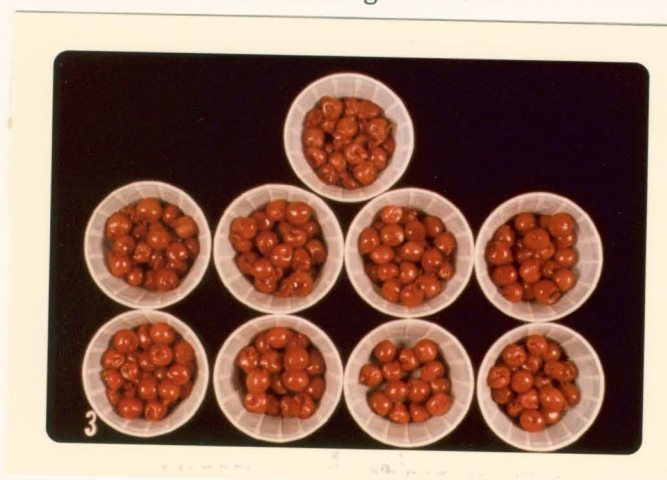
Aroma values of canned Montmorency cherries decreased as storage time increased from 1, 3 to 5 months at temperatures of 35, 75 and 100 F, respectively. Commercial samples were significantly lower in aroma than all other samples (Table 4). Canned cherries with 250 mg/1 Na-HMP were significantly lower in aroma values than other samples except those with 500 mg/1 salts. Sour cherries processed in distilled water had highest aroma values (Table 7).

### Fruit color

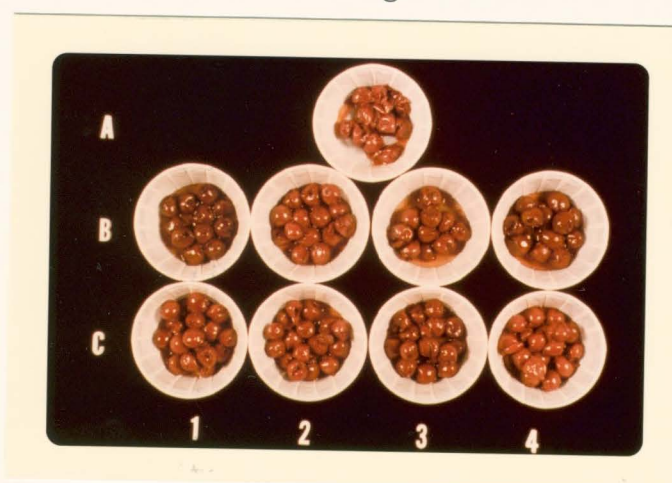
Canned Montmorency cherry color acceptability decreased as storage time and temperature increased among the three storage groups. Cherries processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  were significantly better in color value than cherries processed commercially or in hard or tap waters or water with 250 mg/1 calcium phytate. Those processed with 250 mg/1 Na-HMP were significantly better than those processed in hard (500 mg/1) water (Table 7; Figure 8).



1 month storage at 35 F



3 month storage at 75 F



5 month storage at 100 F

Figure 8. Effects of water quality and temperature and duration of storage on appearance of canned Montmorency cherries. Row a: commercial cherry sample. Row b: tap, distilled, 300 mg/l and 500 mg/l salts water-processed samples. Row c:  $\text{CaNa}_2\text{EDTA}$ , Ca Phytate, Na-HMP and citrate-treated samples.



### Syrup color

Syrup from canned Montmorency cherries decreased significantly in color acceptability as storage increased from 1, 3 to 5 months at 35, 75 and 100 F, respectively (Table 4). Cherry syrup with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  was significantly better in color than all other syrups except those with 500 mg/1 salts or those made with distilled water (Table 7). Cherries processed commercially were poorer in syrup color than laboratory-processed cherries.

### Effects of Water Quality on Physical Characteristics on

#### Canned Blue Lake Green Beans

### Shear values

Commercial samples of canned Blue Lake green beans had significantly higher shear values than laboratory-processed beans while samples processed in distilled water had significantly lower values than those with other treatments according to Duncan's Multiple Mean Comparison Range Test (Tables 5 and 7). Canned green beans processed in hard or tap waters had significantly higher shear values than those processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$ , ascorbic acid or Na-HMP.

### Turbidity, percent light transmittance

Green beans processed with 250 mg/1 ascorbic acid were significantly less turbid than those processed with other treatments except 250 mg/1  $\text{CaNa}_2\text{EDTA}$ . Commercially processed beans were significantly more turbid than all other samples and those processed in tap water were significantly more



Table 5. Effects of water quality on physical, chemical and organoleptic characteristics of canned Blue Lake green beans

Water Quality <sup>a</sup>	Tap	Distilled	500 mg/l salts	CaNa <sub>2</sub> EDTA	Na-HMP	Ascorbic acid	Commercial	F Values
<u>Physical Characteristics</u>								
Shear Values lbs/sq in/50 g	53.5	37.5	56.7	44.2	48.3	44.2	63.3	24.3**
Turbidity, % Light Transmittance	65.2	82.0	76.2	83.7	79.7	85.2	44.3	278.4**
Hunter Color Reflectance (Rd)	22.0	24.9	23.3	27.8	26.4	25.7	25.0	60.0**
Greenness (-a)	5.6	6.9	5.4	8.5	7.0	7.3	5.6	57.6**
Yellowness (b)	11.3	12.3	11.3	13.8	12.8	12.9	12.6	28.2**
<u>Chemical Characteristics</u>								
VRS, µeq/50 g	527	593	756	721	396	654	1017	20.5**
<u>Organoleptic Characteristics</u>								
Firmness <sup>b</sup>	5.0	4.2	4.8	4.1	4.1	5.0	5.5	22.8**
Shape <sup>c</sup>	6.4	4.7	6.4	4.3	4.3	6.1	7.4	22.3**
Turbidity <sup>c</sup>	5.1	6.6	5.6	7.1	4.4	6.7	4.3	43.6**
Flavor <sup>c</sup>	6.5	5.3	5.0	5.5	5.3	6.2	5.7	11.1**
Aroma <sup>c</sup>	5.5	5.5	5.4	5.6	5.5	6.2	5.3	3.3*
Bean Color <sup>c</sup>	5.6	5.9	6.6	6.1	5.7	6.7	5.4	10.0**
Brine Color <sup>c</sup>	5.8	6.1	5.3	7.1	5.2	7.2	4.7	32.1**

<sup>a</sup>See Table 1 for explanation of water qualities.

<sup>b</sup>Subjective evaluation: 9 = extremely firm, 5 = optimum texture, 1 = completely mushy and disintegrating.

<sup>c</sup>Subjective evaluation: 9 = completely acceptable, 1 = completely unacceptable.

\*\*Significance at .01 level F = 3.83.

\*Significance at .05 level F = 2.81.

turbid than other beans processed in the laboratory. Beans canned with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  or distilled water were significantly less turbid than those processed in hard water or with 250 mg/1 Na-HMP (Tables 5 and 7).

#### Hunter color values

Green beans processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  were significantly higher in light reflectance and yellowness than all other samples. Canned green beans with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  or ascorbic acid were significantly more green than other samples. Beans processed in tap or hard water or canned commercially were significantly lower in greenness than were other samples. Those processed in tap or hard waters were significantly lower in light reflectance and yellowness than other samples (Tables 5 and 7).

#### Effects of Water Quality on Chemical Characteristics of Canned Blue Lake Green Beans

##### Volatile reducing substances

Commercially processed Blue Lake green beans were significantly higher in volatile reducing substances than laboratory-processed green beans. Beans processed with 250 mg/1 Na-HMP were significantly lower in VRS than other samples. Those processed in tap or distilled waters were significantly lower than those processed in hard water or with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  (Tables 5 and 7).

## Effects of Water Quality on Organoleptic Characteristics

### of Canned Blue Lake Green Beans

#### Firmness and shape

Commercially processed green beans were significantly firmer and had higher shape scores than all other samples. Beans processed in tap or hard water or with 250 mg/1 ascorbic acid were significantly firmer and of better shape than those processed in distilled water or with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  or Na-HMP (Tables 5 and 7).

#### Turbidity

Blue Lake green beans processed with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  were significantly less turbid than all other samples except those with 250 mg/1 ascorbic acid. Those processed with ascorbic acid and distilled water were significantly less turbid than commercial samples or those processed in tap or hard water or with 250 mg/1 Na-HMP (Tables 5 and 7).

#### Flavor

Blue Lake green beans processed with tap water or 250 mg/1 ascorbic acid were significantly better in flavor than other samples. Those processed in hard water were least acceptable in flavor and significantly poorer than commercially processed samples and those with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  (Tables 5 and 7).

### Aroma

Green beans processed with 250 mg/1 ascorbic acid were significantly better in aroma than all other samples. Those canned commercially and with hard water ranked lowest (Tables 5 and 7).

### Green bean color

Blue Lake green beans canned in hard water or with 250 mg/1 ascorbic acid were significantly better in color value than other samples. Those with 250 mg/1  $\text{CaNa}_2\text{EDTA}$  were also significantly better than commercial, tap or Na-HMP processed green beans (Tables 5 and 7).

### Brine color

Brine from Blue Lake green beans processed with 250 mg/1 ascorbic acid or  $\text{CaNa}_2\text{EDTA}$  were significantly better in color than other brines. Brine from commercially canned beans was significantly lower in color value than other brines. Brines made from distilled or tap waters were significantly better in color than those made with hard water or with 250 mg/1 Na-HMP (Tables 5 and 7).

## DISCUSSION

Physical Characteristics of Canned Apples,  
Sour Cherries and Green Beans

Cell walls of edible plant material are composed of a thin cellulose layer. Parenchyma cells are held together by pectic substances of the middle lamellae and any processing which reacts on either the pectic substances or on the cellulose of the cell wall will affect product texture (Whittenberger, 1952; Weier and Stocking, 1949) as evidenced by differences in shear values in this study.

Histological studies by Strohmaier (1956) showed separation of skin of frozen green beans resulted from breakdown in a layer of large thin-walled parenchyma cells outside the vascular region of the pod. Sistruck and Cain (1960) reported variety, temperature and time of blanch and size of beans affect resistance to epidermal breakdown. Post-harvest storage of fresh beans, longer blanch at lower temperatures (170 to 180 F for 1.5 to 5 minutes) and holding blanched beans hot were recommended to reduce slough. In the present study, blanching for 2.5 minutes at 190 F was employed. The severe sloughing and splitting evidenced when 250 mg/l  $\text{CaNa}_2\text{EDTA}$  and Na-HMP were added to green beans before processing might have been lessened by using a lower blanching temperature. Kaczmarzyk, Fennema and Powrie (1963) found that calcium lactate soak reduced slough while Van Buren and workers (1960)

recommended soaking beans in calcium chloride. These practices might be questioned since the present study showed that beans processed in water with 250 mg/l calcium chloride or in tap water were significantly lower in greenness, light reflectance, yellowness and clarity than other samples.

Plain tin cans are used to pack apples because a slight bleaching effect of tin yields a light-colored product. Neubert and Mottern (1940) found fruit-enamel cans resulted in darker applesauce, especially around air pockets, and in less uniform color. In this study, a decrease in redness and yellowness as apple storage increased from 1 month at 35 F to 3 months at 75 F was observed. Since enameled cans were used for processing cherries and green beans, no observations could be made for these products.

Throughout its history, canned applesauce in metal containers has frequently exhibited headspace corrosion, marked by discoloration of the product and localized severe container detinning (Kohn and Fix, 1956). This type of detinning was noted in apple cans, particularly those used to process Jonathan apple slices. Container detinning increased with increasing storage time (1-4 months) and temperature (35-100 F). This is in agreement with results reported by Lambeth and workers (1967) who found three times as much detinning at 91 F as at 74-78 F. In some cases (Delicious apples with added EDTA and Jonathan samples with copper salts) better color values were noted if cans were more corroded. Chandler and Clegg (1970) showed that the addition of stannous ions to pear puree susceptible to pinking partly or completely inhibited discoloration if added prior to processing. A similar internal environment may

have been present in this study or the reported conditions favored can-ion reaction rather than pigment-ion reactions.

### Chemical Characteristics of Canned Apples,

#### Sour Cherries and Green Beans

##### Calcium pectate and texture

Degradation of texture is caused by an increase in hydrogen ions in the liquid which accelerates hydrolysis and oxidation processes during storage and by breakdown of pectins and calcium pectate (Chiang, 1970) through either high temperature and duration of storage or by chemical treatment. Pectic substances have been defined as a group of complex, colloidal carbohydrate derivatives with a large proportion of anhydrogalacturonic acid units thought to exist in a chain-like combination (Braverman, 1963). A decrease in calcium pectate values with increasing storage temperature and duration was observed for apples with two exceptions; however, calcium pectate values increased with increasing storage for sour cherries. This does not agree with results of Dalal (1963) who found a rapid decrease in pectin content of stored sour cherries and apricots with increasing time (up to 16 weeks) and temperature (40 to 120 F). He hypothesized that decrease in pectin content in stored fruits might be attributable to conversion of protopectin to water-soluble uronic acids. No explanation for the increase in calcium pectate in cherries is proposed particularly since physical and organoleptic measurements of cherry firmness indicated a decrease in this characteristic with increasing storage duration and temperature.



Processing in hard water is actually chemical treatment with minerals. Firming of apples, cherries and green beans by hard water processing was observed in this study and has also been shown by Holgate and Kertesz (1948) and Collins and Wiley (1967). The firming effect of calcium, magnesium and barium salts on plant products low in protein and rich in pectin is due to formation of insoluble pectates in the middle lamellae of cell tissue (Simpson et al., 1955; Weier and Stocking, 1949). Less firming was noted in Jonathan than in Delicious apple slices which agrees with Reeve and Leinbach (1953) who found addition of calcium chloride did not firm tissue of naturally soft apples as much as it did those which were already firm.

Pectin methylesterase (PME) is responsible for desirable textural properties in canned green beans (Kaczmarzyk, Fennema and Powrie, 1963). PME catalyzes the removal of methyl groups from pectic substances, allowing calcium ions to react with exposed carbonyl groups.

Addition of 250 mg/1 CaNa<sub>2</sub>EDTA protected Delicious apple slices against textural degradation at 100 F storage, but was ineffective for Jonathan apple slices or Montmorency cherries. Total acidity values for Montmorency cherries were twice as high as for Jonathan apples which were three times as high as for Delicious samples; it is postulated that acidity was responsible for the ineffectiveness of EDTA treatment at the level used. Correlations of acidity with other chemical, physical and organoleptic characteristics are found in Appendix (Table 6).

### Pigment and color

All apple and cherry samples except Delicious apple slices with 250 mg/1 CaNa<sub>2</sub>EDTA deteriorated significantly for all color-related measurements including pigment after 4 month storage at 100 F. This is in agreement with results reported by Dalal (1963) and by Desrosier (1963) who reported that 50 F was the most desirable storage temperature for canned foods; an increase in temperature to 68 F halved storage life and an increase to 86 F, halved life of those stored at 68 F. Luh and Kamber (1963) stored canned applesauce at temperatures ranging from 32 to 98 F. Undesirable chemical and color changes occurred rapidly at 86 and 98 F. Quality deterioration was related to hydroxymethyl furfural formation and sucrose inversion. It is postulated that this type of non-enzymatic browning was responsible for apple and sour cherry deterioration during 100 F storage. Braverman (1963) and Meyer (1960) explain the chemical reactions involved in carbohydrate and carbohydrate derivative decomposition. Very active aldehydes are formed by three successive dehydrations from reducing sugars, by oxidation of ascorbic acid or by breakdown of other carbohydrates, finally forming hydroxymethyl furfural. This polymerizes with amino groups to cause browning. Pectin, also a carbohydrate, has been found to break upon high-temperature storage releasing galacturonic acid which caused color changes (Stadtman, 1948). The dark brown compounds formed from cherries led the author to suspect the situation described by Markakis, Livingston and Fellers (1957) in which breakdown of anthocyanin involved the hydrolytic opening of the pyrylium ring with the formation of substituted brown insoluble polyphenolic compounds. Although they reported

this condition only at temperatures ranging from 113-230 F, it is possible that the high acidity of the sour cherries combined with the water-soluble pigment and increased susceptibility.

The water soluble pigments (flavones in apples and anthocyanins in cherries) present in the cell sap are greatly affected by metallic ions and salts, according to Braverman (1963). Enzyme-catalyzed oxidative discoloration may explain color degradation of apples and cherries canned in hard water. The most widely accepted theory involves the reaction of polyphenol oxidase (also referred to as polyphenolase and phenolase) with oxygen and suitable substrate of the O-dihydroxyl group, such as caffeic acid or catechol tannins (Joslyn and Ponting, 1950). Earlier theories involving peroxidases, catalase and cytochromes have been largely discounted. A series of related compounds, rather than a single enzyme, seems to be involved (Constantides and Bedford, 1967). Although the mechanism of this reaction is still not proven nor agreed upon, some feel that unsaturated lipids, even though present in only minute amounts, may serve as substrates for oxidative storage degradation changes (Aylward and Haisman, 1969). On the other hand, Reed reported in 1966 that molecular oxygen is the hydrogen acceptor and phenols, the hydrogen donor in the polyphenolase reaction. Monohydric phenols reacting with oxygen yield O-phenols, then O-diphenol plus oxygen give O-quinone and water. Secondary hydroxylation may occur with possible intramolecular rearrangements. Reed feels the browning is the result of polymerization or oxidative polymerization of quinone formed from these mono or di-hydroxyphenols. The enzyme is widely distributed in plants. One atom of copper is incorporated in the molecule and is necessary

for its action; optimum pH of the reaction is between pH 5-7, higher than the pH of canned apples. A gradual slowing down of the action is felt to be due to a free radical which forms an inactive peroxidase. Chlorogenic acid has been implicated as the most important substrate in apple browning caused by polyphenol oxidase (Muneta, 1967).

Inhibitors of polyphenolase are several. The simplest is heat inactivation of the enzyme, but this may ruin texture or flavor of some products. Removal of oxygen from fruit tissue and atmosphere; addition of acid to reduce pH and polyphenolase activity; antioxidants or reducing agents to limit free oxygen or inhibit polyphenolase; and other inhibitors, such as sulfur dioxide; tying up substrate by methylation and genetic control have all been suggested (Ponting, 1960; Reed, 1966; Braverman, 1963; Joslyn and Ponting, 1950). The higher acidity of Jonathan samples may have lowered polyphenolase activity, resulting in the higher color values compared with Delicious apple slices stored at 35 and 75 F.

In the current study, EDTA was most effective in preventing undesirable color changes. Hope (1961) reported that addition of ascorbic acid at a rate of 300 mg/lb fruit controlled browning, reduced headspace oxygen and increased ascorbic acid content. In this laboratory preliminary work in 1969 showed citric acid gave better color values than ascorbic acid addition, however ascorbic acid was very effective in the 1970 study in retaining bean greenness.

The mechanism of action of ascorbic acid in prevention of oxidative breakdown of foods involves its own destructive oxidation, but the particular

pathway depends on the redox potential of the system, pH, oxygen present, other oxidants or reductants, trace metals (particularly copper and iron), amount of ascorbic acid, enzymes involved and time of storage (Bauernfeind and Pinkert, 1970). They reported ascorbic acid delayed color oxidation of olives and artichoke hearts, prevented darkening of frozen French fried potatoes, improved color and palatability of canned mushrooms and inhibited discoloration in processed cauliflower and darkening in processed beets.

Culpepper and Caldwell (1927) reported that stannous chloride and aluminum turned anthocyanin pigments purple and ferric chloride, black. Kitson and Strachan (1955) showed that 2000 ppm calcium phytate inhibited discoloration due to added copper sulfate in Royal Ann cherries, but phytate did not reduce ion adsorption. EDTA (1000 ppm) was not effective in preventing discoloration of Ponceau-dyed fruit canned in aluminum, however 250 ppm calcium phytate was. In the current study, phytate was not as effective as  $\text{CaNa}_2\text{EDTA}$  or Na-HMP at the level of 250 mg/l in retaining color, possibly due to a difference in reaction of natural cherry pigments and dyes or in level of sequestrant used in different studies.

Sistruck and Cash (1968) reported that EDTA prevented ascorbic acid loss but did not maintain color in frozen strawberry puree; they found that stannic chloride provided more color protection than EDTA. Lowering pH to below 3.5 was the most effective method of retaining color of frozen strawberries (Sistruck and Cash, 1968; Wrolstad, Putnam and Varseveld, 1970). Chiang (1970) found that EDTA and Na-HMP (500 ppm) offered more protection for

sweet cherry pigments than processing in distilled or hard (20-160 ppm) water. The increased total acidity in sour cherries over sweet cherries might explain the ineffectiveness of EDTA with sour cherries, particularly since less EDTA was used in the sour cherry study.

The chemical reactions of chlorophyll in green beans are entirely different from those of the water-soluble pigments. Degradation of chlorophyll in canned green beans is caused by pheophytin formation through removal of magnesium from the chlorophyll molecule. MacKinney and Weast (1940) postulated that pheophytin formation was caused by interaction of plant acids with chlorophyll which, although still located in the chloroplast, was no longer protected by the plastid's membrane from the aqueous environment. Blair and Ayres (1943) further confirmed the chemical reactions in pheophytin formation. Chlorophyll retention after blanching decreased as blanching time and temperature increased (Foda, El-Waraki and Zaid, 1968). This author found no specific reference in the literature to increased pheophytin formation in hard water. The results observed were not expected since chlorophyll is a water-insoluble pigment.

#### Nitrate-nitrogen content

Hoff and Wilcox (1970) reported that tomatoes grown under conditions to achieve high accumulation of nitrate caused extensive detinning of internal can surfaces after processing and storage at room temperature for 6 months. This is in agreement with work on citrate and beverage models (Farrow, Lao and Kim, 1970; Johnson, 1970) and canned orange and tomato juices (Horio,

Iwamoto and Oda, 1966; Iwamoto et al., 1967). In the present study, nitrate-nitrogen values were similar for all samples stored 1 month at 35 F, then nitrate values decreased with storage for 3 to 4 months at 75 and 100 F, respectively. More loss was noted for Jonathan than for Delicious apples, a positive correlation with amount of detinning on the can (Table 6).

Farrow, Lao and Kim (1970) showed that ammonia was the principle nitrate reduction product in the pH range of acid products. Nitrous oxide was also produced and acted as an effective detinner at pH 4 and 5, while nitrogen gas may be produced at pH 5; neither would be found in acid apples. These workers found detinning much more rapid in citrate-buffered nitrate solutions as pH decreased. The findings of the present study are in accordance with this, since Jonathan apples were three times as acid as Delicious samples and showed significantly more detinning.

Strodtz and Henry (1954) also showed corrosive action of nitrate toward tin was dependent on the pH of the media for canned green beans, mustard and turnip greens. Farrow, Lao and Kim (1970) showed nitrate-caused corrosion increased rapidly below the pH of 5.2 and 5.5. These results do not agree with those of Horio, Iwamoto and Oda (1966) who found that between the pH of 3 and 5, no difference in detinning was apparent when nitrate content was constant.

A positive logarithmic relationship between initial concentration of nitrate and amount of ammonia detected was observed by Horio, Iwamoto, and Komura (1968) in canned drink model after storage at 38 C. Tin dissolved in



proportion to nitrate concentration. They postulated that when divalent tin, a strong reducing agent, is formed by the action of oxygen, the nitrate present is reduced to nitrite, which readily attacks the metallic tin to form divalent tin, and the reaction proceeds in chain-reaction. Oxygen would be the reaction trigger. This is substantiated by work of Kohn and Fix (1956) who found darkening and corrosion in canned applesauce was due to excessive air in the headspace. It could be controlled by reducing headspace to a minimum and removing air with steam flow, gas flow or vacuum closing.

Organoleptic Characteristics of Canned Apples,  
Sour Cherries and Green Beans

Apples, cherries and green beans processed in hard or tap water generally ranked lower in organoleptic testing than did samples processed with sequestering agents. Griswold (1944a) reported that stannous chloride, calcium chloride and citric acid all lowered canned sour cherry palatability and Chiang (1970) reported that the addition of 500 ppm  $\text{CaNa}_2\text{EDTA}$  or Na-HMP to canned sweet cherries before processing improved organoleptic quality of fruits compared to those processed in distilled water or hard (20 to 160 ppm) water. Holgate and Kertesz (1948) reported that calcium chloride caused objectionable bitterness and saltiness when added to firm canned and frozen apples.

Luh and Kamber (1963) reported that can corrosion in canned applesauce stored above 68 F resulted in released tin and iron which caused flavor and color deterioration of the sauce. This was also noted in the present study.

Correlation coefficients of corrosion with other factors are found in Table 6.

Canned Jonathan apple slices gave higher flavor and volatile reducing substances but lower aroma values than Delicious samples. VRS increased with storage for Jonathan apple slices and for some Delicious apple samples, while it decreased with storage (1 to 3 months at 35 and 75 F, respectively) for Montmorency cherries. Luh (1961) reported that VRS increased as aroma scores increased for canned apricots. He stated that volatile reducing substances might be a valuable aid in evaluating flavor and aroma intensity; however this study shows that intensity might not be correlated positively with acceptability. For example, commercially canned green beans were high in VRS and yet organoleptic judges indicated that aroma was intense and disagreeable. Furthermore, in this study, flavor of Jonathan samples generally was preferred to that of Delicious apple slices while aroma of Delicious apples was preferred to aroma of Jonathan samples.

Green beans processed with ascorbic acid ranked at or near the top for all organoleptic tests for that product. Ascorbic acid addition would also improve nutritional value, although the vitamin C content was not measured in this study. Thiessen (1949) reported that blanching and cutting of beans resulted in great losses of this vitamin, up to 71.4 percent in French cut and 44 percent in 1 inch cut beans. She recommended addition of ascorbic acid to blanch or processing water. Brenner, Wodicka and Dunlop (1948) reported losses of thiamine and ascorbic acid in canned green beans were greater than losses for other nutrients; longer storage at higher temperatures accelerated loss.

Ascorbic acid loss was reported in peas blanched in hard water (Lee and Whitcombe, 1945). The 1965 survey of food consumption of households in the United States revealed that vitamin A and C intake has decreased since 1955 (Economics Research Service, 1967; LeBovit, 1968). The nutritional advantages of ascorbic acid addition plus organoleptic improvement merit consideration.

## SUMMARY AND CONCLUSIONS

The effect of processing water quality, specifically calcium and magnesium hardness (0-500 mg/1) and the addition of chelating agents (0-250 mg/1 of aminopolycarboxylic acids, polyphosphates, hydroxycarboxylic acids and phytates), upon physical, chemical and organoleptic characteristics of canned Jonathan and Delicious apple slices, Montmorency sour cherries and Blue Lake green beans was investigated.

Physical determinations: shear values, turbidity of syrup or brine measured by light transmittance, Hunter color and color difference meter readings and internal can corrosion; chemical composition: pectin as calcium pectate, volatile reducing substances, total acidity, pigment determinations, nitrate-nitrogen values; and sensory measurements: texture, shape, flavor, aroma, color value and uniformity of product and color value and turbidity of product syrup or brine were ascertained.

### Canned Delicious and Jonathan Apple Slices

Use of hard water (300 mg/1 calcium and magnesium salts) as a processing medium for canned apple slices decreased color and flavor scores but increased firmness and shear values. Can corrosion was accelerated and color was unacceptable in the presence of copper and iron impurities, particularly for Jonathan apple slices. Addition of 250 mg/1  $\text{CaNa}_2\text{EDTA}$  to Delicious apple slices canned in water containing 300 mg/1 salts improved

color and flavor while firmness was retained. Water quality control is necessary for maximum canned apple slice acceptability. Methods for water treatment are well summarized in Boby and Solt (1965).

Quality deterioration was evident when apples were stored at 100 F for 4 months; however,  $\text{CaNa}_2\text{EDTA}$  treatment retarded or prevented degradation in Delicious apple slices. EDTA was ineffective in maintaining or improving Jonathan apple quality after 4 month storage at 100 F, probably due to high acidity in the Jonathan cultivar. Internal can corrosion increased markedly when apples were stored at 100 F and was more pronounced at 75 than 35 F storage. As corrosion increased, the values for nitrate-nitrogen, shear, firmness, flavor, aroma, pigment and yellowness decreased. It is recommended that temperatures below 75 F be employed for canned apple product storage.

Delicious apple slices were firmer, had higher shear, nitrate-nitrogen and aroma scores and caused less detinning than Jonathan samples in all storage groups. Color values judged subjectively, reflectance, flavor and volatile reducing substances were higher and redness lower for Jonathan apple slices than for Delicious samples stored at 35 and 75 F for 1 and 3 months, respectively, but not necessarily for samples stored at 100 F for 4 months. Addition of  $\text{CaNa}_2\text{EDTA}$  to Delicious apple syrup improved color and flavor for all storage groups compared to non-treated samples and gave commercially acceptable products even though no soak or blanch pre-treatment was applied.

### Canned Montmorency Cherries

Use of hard (300 and 500 mg/l) water as a canning medium was detrimental to Montmorency cherry palatability, particularly color, flavor and aroma, caused more syrup turbidity, and lowered reflectance, redness, yellowness and anthocyanin values. Excessive hardness toughened the fruit epidermis, making texture undesirable, although firmness is a desirable characteristic in sour cherries. No one sequestering agent used in this experiment resulted in markedly superior products, possibly because sour cherries were so low in pH that 250 mg/l  $\text{CaNa}_2\text{EDTA}$  was ineffective. EDTA did provide most color protection and citric acid, the best flavor and aroma scores.

Hard water is used in all facets of cherry processing, including a 12-15 hour soak before pitting. More differences among treatments might have been evident if different treatment waters had been used for the soak period as well as for packing medium. Bedford and Robertson (1957) reported that calcium chloride-soaked cherries gave significantly lower yield of pitted cherries than when lactate, gluconate, sulfate or citrate were added. Therefore, using soft water in canning plants would prevent economic and quality loss in several ways. This statement is further strengthened by noting that commercially canned sour cherry samples analyzed with laboratory-processed cherries stored at 75 F were poorer than all experimental samples in every test conducted.

As Dalal (1963) reported previously, high temperature storage resulted in decreased product acceptability. In this study, no treatment produced

commercially acceptable cherries when stored at 100 F for 5 months. Commercial and tap water processed sour cherries showed most deterioration whereas cherries with 250 mg/1 CaNa<sub>2</sub>EDTA were most acceptable. One-third of the commercially processed cans stored at 100 F developed springers before the end of 5 months. When comparing storage for 1 month at 35 F versus 3 months at 75 F, analyses of variance showed significant differences for every characteristic measured except texture judged subjectively.

#### Canned Blue Lake Green Beans

Blue Lake green beans canned using distilled water or with 250 mg/1 CaNa<sub>2</sub>EDTA had higher color and greenness values, less turbidity, generally better flavor and aroma, but lower shear, shape and firmness scores than tap or hard water or commercially processed green beans. Addition of 250 mg/1 ascorbic acid to hard water used to process green beans retained greenness, clarity of brine, flavor and aroma while reducing slough and splitting of pods when products were stored 4 months at 75 F. Addition of ascorbic acid also improves nutritive value of the vegetable.

The interrelationships of blanching, calcium salts and ascorbic acid on color and texture of green beans require more study.



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APPENDIX

NAME: \_\_\_\_\_

DATE: \_\_\_\_\_

APPLE PALATABILITY SCORECARD  
(Please grade products in booth under colored light)

Characteristics	Samples					
	1	2	3	4	5	6
FLAVOR: as nearly as possible the flavor of cooked apple. no off flavors. pleasing intensity.						
TEXTURE: firm but tender. not soft, mushy nor rubbery.						
AROMA: pleasing and characteristic of apple.						

COMMENTS:

FLAVOR AND AROMA LEGEND:

TEXTURE LEGEND:

- 9--completely acceptable
- 8--very acceptable
- 7--moderately acceptable
- 6--slightly acceptable
- 5--acceptable
- 4--slightly unacceptable
- 3--moderately unacceptable
- 2--very unacceptable
- 1--completely unacceptable

- 9--extremely hard or rubbery
- 8--very hard, rubbery
- 7--hard or rubbery
- 6--slightly hard or rubbery
- 5--optimum texture
- 4--slightly soft
- 3--soft
- 2--very soft and mushy
- 1--extremely soft and disintegrating

Figure 9. Scorecard used for evaluation of palatability of canned Jonathan and Delicious apple slices.

APPLE APPEARANCE SCORECARD

NAME: \_\_\_\_\_

DATE: \_\_\_\_\_

Characteristics	Samples					
	1	2	3	4	5	6
<p>FRUIT:</p> <p><u>Color Value and Intensity:</u> lustrous, attractive cream color neither dull nor darkened.</p>						
<p><u>Color Uniformity:</u> similar among fruits and within slices.</p>						
<p><u>Shape</u> attractive; no sloughing nor ragged edges; neither shriv- eled nor disintegrating.</p>						
<p>LIQUOR:</p> <p><u>Color Value and Intensity:</u> attractive, nearly colorless. natural for canned apples.</p>						
<p><u>Turbidity:</u> free from sediment and cloudiness.</p>						

COMMENTS:

Scoring Legend: 9--completely acceptable  
 8--very acceptable  
 7--moderately acceptable  
 6--slightly acceptable  
 5--acceptable  
 4--slightly unacceptable  
 3--moderately unacceptable  
 2--very unacceptable  
 1--totally unacceptable

Figure 10. Scorecard used for evaluation of appearance of Jonathan and Delicious apple slices.



NAME: \_\_\_\_\_

DATE: \_\_\_\_\_

CHERRY PALATABILITY SCORECARD  
PLEASE GRADE PRODUCTS IN BOOTH UNDER RED LIGHT

Characteristics	SAMPLES							
	1	2	3	4	5	6	7	8
FLAVOR: as nearly as possible the flavor of cooked fruit. no off flavors. pleasing flavor intensity.								
AROMA: Pleasing and char- acteristic of cherries.								
TEXTURE: Firm but tender, smooth. not soft, mushy nor tough.								

COMMENTS:

FLAVOR AND AROMA SCORING LEGEND:

- 9--completely acceptable
- 8--very acceptable
- 7--moderately acceptable
- 6--slightly acceptable
- 5--acceptable
- 4--slightly unacceptable
- 3--moderately unacceptable
- 2--very unacceptable
- 1--completely unacceptable

TEXTURE LEGEND:

- 9--extremely hard
- 8--very hard
- 7--hard
- 6--slightly hard
- 5--good texture
- 4--slightly soft
- 3--soft
- 2--very soft and mushy
- 1--extremely soft and disintegrating

Figure 11. Scorecard used for evaluation of palatability of canned Montmorency cherries.

NAME: \_\_\_\_\_  
 DATE: \_\_\_\_\_

CHERRY APPEARANCE SCORECARD

Characteristics	Samples							
	1	2	3	4	5	6	7	8
CHERRY FRUIT: <u>Color Value and Intensity:</u> attractive red color, natural for cooked fruit at prime maturity. lustrous, neither faded nor muddy.								
<u>Color Uniformity:</u> similar among fruits.								
<u>Shape:</u> uniform, plump, smooth. neither shriveled nor disintegrating.								
CHERRY LIQUOR: <u>Color Value and Intensity:</u> attractive red hue. natural for cherry.								
<u>Turbidity:</u> free from sediment and cloudiness.								

COMMENTS:

Scoring Legend: 9--completely acceptable      4--slightly unacceptable  
 8--very acceptable                                      3--moderately unacceptable  
 7--moderately acceptable                            2--very unacceptable  
 6--slightly acceptable                                1--totally unacceptable  
 5--acceptable

Figure 12. Scorecard used for evaluation of appearance of canned Montmorency cherries.

NAME: \_\_\_\_\_

DATE: \_\_\_\_\_

GREEN BEAN PALATABILITY SCORECARD  
PLEASE GRADE PRODUCTS IN BOOTH UNDER COLORED LIGHT

Characteristics	Samples							
	1	2	3	4	5	6	7	8
FLAVOR: as nearly as possible the flavor of cooked beans no off flavors. pleasing flavor intensity.								
AROMA: Pleasing and characteristic of beans.								
TEXTURE: firm, but tender. not soft, mushy, tough nor stringy.								

COMMENTS:

FLAVOR AND AROMA SCORING LEGEND:

- 9--completely acceptable
- 8--very acceptable
- 7--moderately acceptable
- 6--slightly acceptable
- 5--acceptable
- 4--slightly unacceptable
- 3--moderately unacceptable
- 2--very unacceptable
- 1--completely unacceptable

TEXTURE LEGEND:

- 9--extremely hard
- 8--very hard
- 7--hard
- 6--slightly hard
- 5--good texture
- 4--slightly soft
- 3--soft
- 2--very soft and mushy
- 1--extremely soft and disintegrating

Figure 13. Scorecard used for evaluation of palatability of canned Blue Lake green beans.

NAME: \_\_\_\_\_

DATE: \_\_\_\_\_

GREEN BEAN APPEARANCE SCORECARD

Characteristics	Samples							
	1	2	3	4	5	6	7	8
<b>VEGETABLE:</b> <u>Color Value and Intensity:</u> attractive natural green color. neither faded nor drab.								
<u>Color Uniformity:</u> similar among fruits.								
<u>Shape:</u> attractive; no sloughing, splitting nor ragged edges.								
<b>LIQUOR:</b> <u>Color Value and Intensity:</u> attractive, pale green. natural for canned beans.								
<u>Turbidity:</u> free from sediment and cloudiness.								

COMMENTS:

Scoring Legend: 9--completely acceptable  
 8--very acceptable  
 7--moderately acceptable  
 6--slightly acceptable  
 5--acceptable  
 4--slightly unacceptable  
 3--moderately unacceptable  
 2--very unacceptable  
 1--totally unacceptable

Figure 14. Scorecard used for evaluation of appearance of canned Blue Lake green beans.

Table 6. Correlation coefficients for selected factors related to quality of canned Delicious and Jonathan apples, Montmorency cherries and Blue Lake green beans

Factor	Correlated with Factor	Values		
		Apple	Cherry	Bean
Firmness	Shear Values	.89	.47	.76
Firmness	Shape	.59		.99
Firmness	Turbidity-objective	.59		-.85
Shape	Shear Values	-.52		.79
Shape	Turbidity-objective	.54	.70	-.44
Shape	Turbidity-subjective	.60	.52	-.84
Shape	Syrup Color	.65		
Turbidity-subjective	Turbidity-objective	.61	.50	.60
Turbidity-subjective	Redness		.75	
Turbidity-subjective	Shear Values			-.80
Flavor	Aroma	.74	.78	.41
Total Acidity	Firmness	-.77		
Total Acidity	Fruit Color	.73		
Total Acidity	Shear Values	-.65		.59
Total Acidity	Corrosion	-.53		
Total Acidity	Nitrate	-.48		
Corrosion	Nitrate	.67		
Corrosion	Shear Values	.76		
Corrosion	Firmness	.71		
Corrosion	Flavor	.56		
Corrosion	Aroma	.58		
Corrosion	Pigment	.66		
Corrosion	Yellowness	.64		
Reflectance	Redness	-.78		-.87
Reflectance	Yellowness	.58	.56	.97
Reflectance	Pigment	.55		
Reflectance	Turbidity-objective	.66		
Redness	Anthocyanins		.67	
Redness	Yellowness			-.86
Fruit Color Value	Redness	.73	.67	-.26
Fruit Color Value	Yellowness	.77	.16	.06
Fruit Color Value	Syrup Color Value	.62	.64	.55
Fruit Color Value	Color Uniformity	.70		
Fruit Color Value	Anthocyanins		.48	
Fruit Color Value	Turbidity-objective	.79		
Fruit Color Value	Turbidity-subjective		.69	
Syrup Color Value	Redness	-.68	.67	-.75
Syrup Color Value	Pigment	.53	.56	
Syrup Color Value	Turbidity-subjective	.89	.87	
Syrup Color Value	Reflectance	.80		.39
Syrup Color Value	Yellowness	.58		

Table 7. Range of significant differences using Duncan's Multiple Mean Comparison Range Test for canned Montmorency cherry and Blue Lake green bean data

Measurement	Least Significant Range			
	Cherry		Green Bean	
	.05	.01	.05	.01
<u>Physical Measurements</u>				
Shear Values	6.43-7.08	8.45-9.21	4.72-5.39	6.35-7.12
Hunter Color Values				
Reflectance (Rd)	.64-.71	.84-.92	.66-.75	.89-.99
Redness (a)	.83-.92	1.09-1.19	.40-.46	.54-.61
Yellowness (b)	.51-.56	.67-.73	.46-.53	.62-.70
Turbidity, Percent Light Transmittance	3.09-3.40	4.06-.4.42	2.32-2.65	3.12-3.50
<u>Chemical Measurements</u>				
Calcium Pectate	.00241- .00266	.00300- .00345		
Volatile Reducing Substances	14.9-16.4	19.6-21.3	11.5-13.2	15.2-17.4
Anthocyanins	.328-.362	.408-.470		
Total Acidity	.013-.015	.017-.020		
<u>Organoleptic Measurements</u>				
Firmness	.45-.50	.56-.65	.31-.36	.42-.47
Shape	.77-.89	1.01-1.16	.69-.79	.93-1.04
Turbidity	.34-.39	.44-.51	.46-.52	.61-.69
Flavor	.52-.60	.68-.79	.43-.47	.56-.62
Aroma	.43-.50	.56-.65	.43-.49	.58-.64
Fruit Color	.71-.83	.93-1.07	.41-.47	.55-.62
Syrup Color	.36-.39	.50-.51	.45-.51	.60-.68

## VITA

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Doctor of Philosophy

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