Quality of Frozen Apples Related to Variety and Ripeness

JOSEPH S. CALDWELL[1], CHARLES W. CULPEPPER[2], and KENNETH D. DEMAREE
Biological Sciences Branch, Agricultural Marketing Service, U. S. Department of Agriculture, Beltsville, Md.

Sixteen varieties of apples that comprised over 90% of the commercial apple crop of the United States were tested for their relative suitability for freezing and the effect of ripeness on the quality of the frozen product. Fruit harvested at the firm ripe stage of maturity and frozen without further ripening was inferior in flavor to fruit ripened to a good edible stage before freezing. In most cases the use of an antioxidant was necessary to prevent excessive browning. Overripeness resulted in a soft, mushy texture which calcium chloride treatment did not prevent. In general, Jonathan, Yellow Newtown, Golden Delicious, and York Imperial were considered best for freezing.

Studies on the preservation of apples by freezing have dealt largely with varieties grown in excess of what the fresh market would take at profitable prices. Consequently they have concentrated largely on methods of using surplus stocks rather than on determining which varieties are best adapted to freezing. The present work extending over 3 years was undertaken to study relative suitability for freezing of the important commercial varieties; effect of degree of ripeness on the frozen product, with special reference to the amount of disintegration, susceptibility to browning, and flavor of the product; and methods of preventing browning and disintegration in order to utilize fruit that might otherwise be unsuitable for freezing.

Materials and Methods

Sixteen varieties which made up over 90% of the commercial apple crop of the United States in the years 1945 to 1947 were included in the study (*1*). Ten of the varieties were obtained from the orchards of the Plant Industry Station, Beltsville, Md., or from commercial orchards in nearby Maryland or Virginia, and were used throughout the study. The other six varieties were not available locally and were obtained from other areas and tested only 1 year. These were Cortland from New York and Massachusetts, Golden Delicious from Ohio, McIntosh and Rhode Island Greening from New York, Northern Spy from Michigan and New York, and Turley from Ohio. Baldwin from New York and Grimes Golden and Jonathan from Ohio were used for comparison with locally grown apples of the same varieties.

Fruit grown at Beltsville or in nearby Maryland and Virginia orchards was harvested at the firm ripe stage of maturity and placed in storage at 32° F. on the day harvested. Fruit from distant areas was similarly harvested, shipped by express to Beltsville, and placed at 32° on arrival. The locally grown fruit and most of that from other areas met the maturity standards recommended for the variety as measured by the Magness-Taylor pressure test. The pressure tests for a few lots from distant areas were lower than recommended when received at Beltsville. Most of the fruit was harvested between September 22 and October 12, but a few later-maturing varieties were harvested up to October 27.

Within 3 days after receipt of a variety, approximately 50 pounds of the fruit were prepared for freezing (pack 1). The remainder was held for 2 or more weeks at 32° F. until time permitted processing it. At this time the remainder of each lot or variety was transferred to 70° F. and allowed to ripen. A second pack was prepared one week after transfer. Further packs were prepared at weekly intervals until the fruit was so overripe that it could no longer be used. The packs were consecutively numbered.

Before the fruit was prepared for freezing, ripeness or firmness was determined by use of the Magness-Taylor pressure tester. It was then peeled, cored, and halved and the halves were sliced mechanically into $^3/_8$-inch half-moon-shaped slices. The slices were held in cold water until ready to pack into 2-pound waxed cardboard cartons having heat-sealable vaporproof inner bags. The slices were packed without additional treatment, packed with 50% sugar sirup, and packed with various antioxidants and firming agents at different concentrations and for varying periods. The sealed packages were frozen by placing them on a wire-mesh tray in a room held at −15° F. Subsequent storage was at −7° to −10°. All lots had been processed by December 24, and were held in frozen storage for 24 weeks after that date before examination of the frozen product began.

The processed material was examined and evaluated for color and general appearance in the frozen state and for degree of discoloration after thawing. Comparable frozen samples were placed in flowing steam for 30 minutes, and the cooked product was rated for color, flavor, texture, and fragmentation of pieces and disintegration of tissues. Each factor was rated numerically, 1 to 1.9 denoted excellent, 2 to 3.5 very good to good, 3.6 to 4.9 fair to poor, 5 to 6 barely or doubtfully acceptable, and above 6 unacceptable. In so far as practicable, samples were selected for examination so that different varieties and treatments could be compared directly and differences readily observed.

Varietal Behavior during Ripening

The varieties used, the states where they were grown, and the pressure tests results at time of preparation for freezing are given in Table I. The judges' ratings (averages) for fruit packed in 50% sugar sirup without antioxidants or firming agents, together with the flavor ratings for material treated with potassium metabisulfite and ascorbic acid to reduce discoloration, are included.

The flavor of the processed product improved as the raw product ripened to a good edible stage. The fruit packed at the firm ripe stage of maturity was so astringent and lacking in flavor that a number of samples were considered doubtfully acceptable for this reason. Even the overripe fruit still possessed good flavor, although excessive fragmentation and disintegration are factors in such fruit.

[1] Deceased.
[2] Present address, Arlington, Va.

Table I. Color, Flavor, and Disintegration of Frozen Apples as Related to Variety and Stage of Ripeness When Packed[a]

Variety	Source	Pack No.	Pressure Test, Lb.	Raw Product Color: Frozen	Raw Product Color: Thawed	Cooked Product: Color	Cooked Product: Disintegration	Cooked Product Flavor: No antioxidant	Cooked Product Flavor: Potassium meta-bisulfate–treated	Cooked Product Flavor: Ascorbic acid–treated
Baldwin	Md.	1	16.5	6.1	7.3	5.2	1.2	4.4	4.6	4.5
		2	13.5	3.8	4.5	3.5	2.4	2.6	4.1	2.6
		3	10.6	...	...	3.6	...	...	4.8	2.3
		4	9.8	3.7	...	3.2	2.5	1.9	4.0	2.2
	N. Y.	1	17.0	4.3	6.3	2.3	1.5	2.3	4.0	2.6
		2	12.2	4.5	5.6	3.8	6.0	2.5	3.7	2.9
		3	9.9	5.1	4.5	4.1	5.0	2.4	4.6	2.5
		4	7.9	4.7	4.6	3.8	6.2	3.1	5.6	2.7
Cortland	Mass.	1	10.2	3.7	4.3	3.6	3.3	3.6	4.3	2.6
		2	7.7	5.3	6.0	4.8	6.4	3.0	5.1	2.5
		3	6.8	2.9	2.5	3.1	4.0	2.3	4.1	2.5
		4	6.9	2.8	3.6	4.3	5.8	1.9	8.3	2.5
	N. Y.	1	11.3	5.0	5.0	4.3	2.5	3.2	4.3	3.0
		2	7.3	3.7	4.3	3.5	4.8	2.9	4.3	2.5
		3	6.8	3.1	3.0	3.6	4.2	2.0	4.8	2.2
Delicious	Md.	1	13.9	4.9	7.5	4.0	1.3	4.4	5.4	3.8
		2	11.6	4.3	4.5	3.8	2.2	3.7	4.7	3.5
		3	9.0	5.0	4.3	5.0	3.8	2.9	4.8	2.8
		4	8.0	4.2	...	5.7	2.7	1.9	4.5	2.0
Golden Delicious	Ohio	1	7.9	4.0	4.6	3.1	2.0	2.7	3.4	2.9
		2	7.3	4.1	4.3	3.0	2.1	3.5	4.6	3.0
Grimes Golden	Md.	1	15.6	2.9	3.5	4.0	1.8	4.3	4.8	4.7
		2	10.6	3.5	4.3	2.8	4.8	4.3	4.9	3.2
		3	8.4	3.0	3.0	2.8	3.6	2.4	4.6	2.6
		4	8.5	4.0	...	3.1	6.0	2.1	4.0	2.6
	Ohio	1	9.7	3.6	6.3	3.5	3.6	3.1	4.2	2.7
		2	9.5	3.6	3.3	3.1	4.3	3.4	3.9	2.8
Jonathan	Md.	1	12.3	1.8	2.0	2.5	2.3	5.0	6.2	...
		2	8.6	3.9	4.7	2.8	1.6	3.0	4.2	3.2
		3	7.9	3.5	4.3	2.5	1.5	2.3	4.9	2.1
		4	7.8	...	...	2.2	...	...	4.7	...
	Ohio	1	8.0	3.7	4.3	2.2	2.1	2.3	3.4	2.5
		2	7.5	2.7	2.6	3.1	2.8	3.2	4.5	2.8
Lowry	Va.	1	16.7	7.2	8.7	8.7	1.1	5.7	5.1	4.8
		2	11.5	5.8	6.2	5.3	3.0	4.8	5.1	3.6
		3	10.0	6.4	4.5	6.4	3.0	2.9	5.0	2.9
		4	8.4	4.2	...	3.7	3.0	2.9	4.2	3.0
McIntosh	N. Y.	1	11.0	6.9	6.6	5.0	5.0	3.5	...	2.3
		2	8.8	4.8	6.7	5.0	6.0	2.5	4.5	2.9
		3	7.4	6.2	6.3	5.9	4.2	2.1	5.0	2.3
		4	7.0	3.3	...	4.2	4.0	1.7	2.7	2.1

Varieties differed in their susceptibility to fragmentation and disintegration even though of comparable firmness when prepared for freezing. Some varieties like Jonathan, Yellow Newtown, Golden Delicious, and York Imperial remained largely intact after cooking, when frozen at all stages of ripeness. McIntosh, Turley, and Cortland underwent extensive disintegration even when packed shortly after harvest.

However, firmness of the raw material is a factor in determining the amount of disintegration that is likely to occur. This is shown in Table II, where the fruit is regrouped according to pressure test at time of preparation. The amount of disintegration progressively increased as the fruit became softer. The flavor improved in the softer fruit except in the metabisulfite-treated samples, in which the softer fruit was more adversely affected by this chemical.

Varieties varied also in their susceptibility to discoloration, both during preparation and freezing and during thawing (Table I). The stage of ripeness was a factor in some varieties, the firmer fruit of Lowry and Rome Beauty tending to discolor more readily than the riper fruit; in others such as Grimes Golden, McIntosh, and York Imperial the stage of ripeness had less effect. If cooking was delayed until thawing began, a greater amount of discoloration occurred. In some varieties, notably Northern Spy, Stayman Winesap, Turley, and Winesap, material improvement in color resulted from cooking, but in others such as Cortland, Lowry, and Rhode Island Greening, the colors of the frozen and the cooked material were about the same.

In Table III the values for the different packs are averaged and the varieties are classified according to flavor of the ascorbic acid–treated material. Tressler and Du Bois (*2*) reported that the ascorbic acid treatment did not affect the flavor, and the fruit did not readily take on off-flavors resulting from oxidation. Discoloration, an important factor in untreated material, can be effectively reduced by suitable antioxidants.

It is evident that varieties differ in their response to freezing preservation and for best results each variety should be considered individually. Freezing at the firm ripe stage of maturity resulted in inferior flavor and is generally inadvisable. The color in some cases was also distinctly improved by ripening, but this was of less importance than improvement in flavor. Discoloration is of sufficient importance to justify preventive measures with all varieties and at all stages of ripeness, and in most cases such measures are necessary if an acceptable product is to be obtained.

Table I (Continued)

Variety	Source	Pack No.	Pressure Test, Lb.	Raw Product Color		Cooked Product				
								Flavor		
				Frozen	Thawed	Color	Disintegration	No antioxidant	Potassium meta-bisulfate-treated	Ascorbic acid-treated
Northern Spy	Mich.	1	14.3	7.3	6.3	4.8	2.1	2.6	4.4	2.8
		2	11.9	6.2	6.6	4.6	3.0	2.2	2.5	2.5
		3	11.3	6.1	5.0	5.3	2.2	1.8	3.4	2.1
		4	9.5	6.6	8.3	5.5	1.7	2.0	4.4	2.7
	N. Y.	1	14.9	4.5	6.3	4.1	2.0	2.6	4.2	3.1
		2	11.8	6.1	5.6	3.8	3.1	3.4	3.6	3.7
		3	9.8	4.1	3.0	3.3	2.2	2.0	4.4	2.6
		4	9.5	5.2	5.6	5.0	2.0	2.7	4.0	2.1
Rhode Island Greening	N. Y.	1	12.9	6.2	5.7	6.4	2.1	5.2	4.9	5.7
		2	10.2	6.0	7.5	6.2	5.2	3.5	3.8	3.0
		3	9.5	6.3	8.6	5.0	4.0	3.6	4.9	3.0
		4	8.7	5.2	...	5.1	3.0	3.1	4.0	3.7
Rome Beauty	Md.	1	16.5	5.0	7.5	5.8	1.3	3.0	4.3	2.4
		2	12.7	5.4	5.5	5.1	2.3	3.7	3.9	3.7
		3	11.8	4.1	5.3	4.5	4.4	2.9	4.4	3.0
		4	10.6	2.2	...	3.0	2.5	2.5	4.3	3.0
Stayman Winesap	Md.	1	16.4	5.9	7.2	4.5	1.7	5.1	5.2	3.1
		2	10.5	5.1	5.5	4.1	2.4	3.5	5.0	3.2
		3	8.5	6.0	7.0	4.6	5.0	3.9	5.4	2.8
		4	7.8	5.0	...	3.7	6.5	3.0	5.0	3.1
Turley	Ohio	1	10.2	5.2	7.6	3.6	5.0	3.1	4.9	2.9
		2	8.7	5.1	6.0	3.5	8.2	2.9	4.6	2.6
		3	8.5	7.0	8.3	4.3	...	5.0	5.7	3.6
Winesap	Va.	1	17.3	4.0	5.0	2.7	1.6	3.2	4.4	3.3
		2	13.0	4.8	5.0	3.0	3.4	5.2	4.8	3.4
		3	10.3	5.1	3.5	3.4	5.0	2.6	4.0	2.4
		4	9.7	3.9	4.3	2.5	4.5	3.5	6.7	4.1
Yellow Newtown	Md.	1	17.4	4.0	6.0	2.4	1.0	2.8	4.0	3.0
		2	16.4	5.0	4.6	2.5	1.2	2.3	3.8	2.6
		3	15.0	2.4	2.6	2.5	1.2	2.0	3.3	...
		4	13.6	4.0	5.0	3.6	1.0	2.1	...	1.9
		5	13.5	3.9	4.6	3.5	1.1	1.9	4.0	1.9
York Imperial	Md.	1	16.3	5.2	6.0	5.1	1.0	4.8	5.9	4.6
		2	15.4	4.0	7.5	4.5	1.6	4.0	4.4	3.6
		3	13.3	3.7	5.3	3.3	2.1	2.8	5.1	2.9
		4	12.0	4.0	...	4.0	1.0	2.1	4.5	2.6
		5	10.9	5.1	5.6	4.3	2.0	2.9	...	2.8
		6	10.4	4.6	6.0	3.2	1.7	2.4	4.8	2.7
Average all lots			10.99	4.62	5.34	4.00	3.09	3.08	4.60	3.02

[a] Mean scores. 1 to 1.9, excellent; 2 to 3.5, very good to good; 3.6 to 4.9, fair to poor; 5 to 6, barely or doubtfully acceptable; above 6, unacceptable.

Effect of Antioxidants

Several materials have been recommended to prevent browning of apples intended for freezing (*3*). Of these sulfur dioxide or sulfurous acid and various salts thereof are effective and widely used, even though in high concentrations they may cause off-flavors. Sulfurous acid penetrates the apple tissues much more rapidly than the sulfites. Freezing stops the penetration, and where sulfites are used, it is necessary to delay freezing the treated material until adequate penetration can take place. In spite of this, sulfite is still preferred by many to sulfurous acid because of ease of handling it and its less offensive odor. Ascorbic and citric acids also have been used. Ascorbic acid, while more expensive than sulfur dioxide, has the decided advantage that excess amounts do not adversely affect the flavor, and any excess is nutritionally beneficial. To determine what effect variety and ripeness have on the effectiveness of antioxidants, various concentrations and periods of treatment were tried.

In general, fruit dipped for 3 minutes in a solution containing 2000 p.p.m. of sulfur dioxide was unacceptable because of excessive bleaching and objectionable taste. When dipped for 1 minute in a solution of this concentration, the fruit

Table II. Color, Flavor, and Disintegration of Frozen Apples (All Packs) as Related to Firmness of Fruit before Freezing[a]

Pressure-Test Group, Lb.	Average Pressure Test, Lb.	Raw Product Color		Cooked Product				
						Flavor		
		Frozen	Thawed	Color	Disintegration	No antioxidant	Potassium meta-bisulfite-treated	Ascorbic acid-treated
15 and over	16.4	4.7	6.0	4.2	1.4	3.7	4.5	3.5
12 to 14.9	13.2	4.5	5.3	4.0	2.2	3.3	4.6	3.1
9 to 11.9	10.4	5.0	5.4	4.2	3.4	3.0	4.4	2.8
Below 9	7.9	4.3	4.8	3.7	4.2	2.7	4.6	2.7

[a] Mean scores. 1 to 1.9, excellent; 2 to 3.5, very good to good; 3.6 to 4.9, fair to poor; 5 to 6, barely or doubtfully acceptable; above 6, unacceptable.

Table III. Varieties (All Packs) Classified According to Flavor Ratings of Frozen Product, Ascorbic Acid Used as Antioxidant[a]

				Raw Product Color		Cooked Product				
								Flavor		
Variety	Source	No. of Packs	Pressure Test, Lb.	Frozen	Thawed	Color	Disintegration	No antioxidant	Potassium metabisulfite-treated	Ascorbic acid-treated
Yellow Newtown	Md.	5	15.2	3.9	4.6[b]	2.9	1.1	2.2	3.8	2.4
McIntosh	N. Y.	4	8.6	5.3	6.5(3)	5.0	4.8	2.4	4.1	2.4
Cortland	Mass.	4	7.9	3.9	4.1	4.0	4.9	2.7	5.4	2.5
Northern Spy	Mich.	4	11.8	6.6	6.6	5.0	2.2	2.2	3.7	2.5
Cortland	N. Y.	3	8.5	3.9	4.1	3.8	3.8	2.7	4.5	2.6
Jonathan	Md.	4	9.2	3.1	3.7(3)	2.6(3)	1.8(3)	3.4(3)	5.0	2.6(2)
Jonathan	Ohio	2	7.8	3.2	3.4	2.6	2.4	2.8	4.0	2.6
Baldwin	N. Y.	4	11.8	4.6	5.2	3.5	4.7	2.6	4.5	2.7
Grimes Golden	Ohio	2	9.6	3.6	4.8	3.3	4.0	3.2	4.0	2:8
Northern Spy	N. Y.	4	11.5	5.0	5.1	4.0	2.3	2.7	4.0	2.9
Baldwin	Md.	4	12.6	4.5(3)	5.9(2)	4.0(3)	2.0(3)	3.0(3)	4.4	2.9
Golden Delicious	Ohio	2	7.6	4.0	4.4	3.0	2.0	3.1	4.0	3.0
Rome Beauty	Md.	4	12.9	4.2	6.1(3)	4.6	2.6	3.0	4.2	3.0
Delicious	Md.	4	10.6	4.6	5.4	4.6	2.5	3.2(2)	4.8	3.0
Turley	Ohio	3	9.1	5.8	7.3	3.8	6.6	3.7	5.1	3.0
Stayman Winesap	Md.	4	10.8	5.5	6.6(3)	4.2	3.9	3.9	5.2	3.0
York Imperial	Md.	6	13.0	4.4	6.1(5)	4.1	1.6	3.2	4.9(5)	3.2
Grimes Golden	Md.	4	10.8	3.4	3.6(3)	3.2	4.0	3.3	4.6	3.3
Winesap	Va.	4	12.6	4.4	4.4	2.9	3.6	3.6	5.0	3.3
Lowry	Va.	4	11.6	5.9	6.5(3)	6.0	2.5	4.1	4.8	3.6
Rhode Island Greening	N. Y.	4	10.3	5.9	7.3(3)	5.7	3.6	3.8	4.4	3.8

[a] Mean scores. 1 to 1.9, excellent; 2 to 3.5, very good to good; 3.6 to 4.9, fair to poor; 5 to 6, barely or doubtfully acceptable; above 6, unacceptable.
[b] Numbers in parentheses indicate number of packs evaluated if different from that indicated under No. of packs.

was free of browning and remained free during thawing and cooking of sauces and pies. However, in most cases the fruit retained sufficient sulfur dioxide to affect the flavor adversely. This became increasingly evident in the riper fruit. A 1-minute dip at a concentration of 1500 p.p.m. resulted in good color in practically all varieties, but the effect on flavor varied with the firmness of the flesh. At a pressure test of 12 to 18 pounds little adverse effect was usually evident, but in softer fruit sulfur dioxide was frequently detected in objectionable amounts. Fruit packed in sirup was usually less affected than that packed without any liquid. From a concentration of 1000 p.p.m. no adverse effect resulted even when the fruit was held for 3 minutes, but some browning occurred in the firmer fruit.

The relative effectiveness of various antioxidants in reducing discoloration of frozen samples packed in 50% sirup is shown in Table IV. Color was determined visually on the cooked product, and the values given are the average of the judges' ratings. In the sulfur dioxide tests, the sliced apples in packs 1 (at harvest) and 2 (ripened 1 week) were dipped for 1 minute in a potassium metabisulfite solution containing 1500 p.p.m. of sulfur dioxide and in later packs for 2 minutes in a solution containing 1000 p.p.m. From preliminary results this procedure appeared to have no adverse effect on the flavor, and it was

Table IV. Effectiveness of Various Antioxidants as Related to Variety and Stage of Ripeness[a]

Variety	Source	Pack No.	Pressure Test, Lb.	Control Untreated	Potassium Meta-bisulfite[b]	Ascorbic Acid[c]	Citric Acid[d]	Ascorbic and Citric Acids[e]
Baldwin	Md.	1	16.5	5.2	4.4	4.6	5.8	2.0
		2	13.5	3.5	1.6	2.2	2.9	2.2
		3	10.6	3.6	2.7	2.6	1.8	2.3
		4	9.8	3.2	1.2	2.2	3.0	2.2
Baldwin	N. Y.	1	17.0	2.3	1.5	1.7	3.3	2.9
		2	12.2	3.8	1.9	3.5	2.2	2.2
		3	9.9	4.1	2.2	2.6	3.6	2.9
		4	7.9	3.8	1.7	2.2	2.2	2.2
Cortland	Mass.	1	10.2	3.6	1.6	1.9	3.0	1.6
		2	7.7	3.6	2.3	2.8	3.0	1.7
		3	6.8	3.6	3.2	2.5	3.2	2.5
		4	6.9	4.3	2.3	2.1	3.2	3.6
Cortland	N. Y.	1	11.3	4.3	1.7	1.7	2.8	1.7
		2	7.3	3.5	2.1	2.5	2.6	1.4
		3	6.8	3.6	2.3	2.3	2.6	2.1
Delicious	Md.	1	13.9	4.0	2.2	3.0	3.7	2.4
		2	11.6	3.8	2.3	2.5	3.3	2.1
		3	9.0	5.0	3.1	3.5	3.8	2.4
		4	8.0	5.7	1.5	2.1	3.2	2.1
Golden Delicious	Ohio	1	7.9	3.1	1.2	1.9	1.9	...
		2	7.3	3.0	1.6	2.0	2.1	...
Grimes Golden	Md.	1	15.6	4.0	2.8	2.5	2.9	2.2
		2	10.6	2.8	1.4	1.6	1.8	1.7
		3	8.4	2.8	2.3	1.6	2.6	1.7
		4	8.5	3.1	1.5	2.0	3.2	2.0
Grimes Golden	Ohio	1	9.7	3.5	1.7	2.3	3.0	...
		2	9.5	3.1	1.5	1.3	2.0	...
Jonathan	Md.	1	12.3	2.5	2.2	2.5	2.7	1.8
		2	8.6	2.8	1.5	1.8	3.2	1.8
		3	7.9	2.5	1.5	2.0	3.5	1.5
		4	7.8	2.2	1.2	2.2	...	...
Jonathan	Ohio	1	8.0	2.2	1.6	1.8	2.5	2.1
		2	7.5	3.1	1.1	1.6	2.6	2.9

followed in later tests. However, as shown in Tables I and II, this treatment often resulted in poorer flavor than that of untreated or ascorbic acid–treated material and thus must be considered above optimum for best results. The potassium metabisulfite–treated fruit was held at room temperature, approximately 70° F., for 4 hours to allow penetration of the sulfur dioxide before it was frozen. The other antioxidants were used as noted in footnotes of Table IV.

It is readily evident that the antioxidants were effective in reducing browning. Sulfur dioxide at the concentration used was very effective. Only in rare instances was the treated material scored below good to very good for color and over half of the samples were rated excellent. In the untreated material only 38% of the samples were rated good or better for color. A limited number of tests indicated that the sulfur dioxide could be added to sirup or water if either is used in the packed fruit. A concentration of 150 p.p.m. in the sirup effectively prevented browning and had little or no effect on the flavor. Lower concentrations were not effective in preventing browning and higher concentrations affected the flavor.

Ascorbic acid used in adequate amounts is also effective in reducing discoloration in apples. Although not quite as effective as sulfur dioxide at the concentrations reported in Table IV, 92% of the samples were rated good or better for color and all were acceptable. Concentrations much below 1 to 2500 were not effective in preventing browning, while 1 to 1000 prevented browning for 5 hours or more during and after thawing of the uncooked material. No adverse effects on flavor result from high concentrations of ascorbic acid.

Citric acid at a concentration of 1 to 1000 of fruit and sirup was less effective in preventing browning than the other antioxidants used, but the percentage of samples treated with it that rated good or better for color was double the untreated samples (77% *vs.* 38%). Higher concentrations than 1 to 1000 of fruit and sirup affected the flavor and lower concentrations were correspondingly less effective in preventing browning.

Various combinations of citric and ascorbic acids were tried. No combination of the two was found that was consistently superior to ascorbic acid alone or that permitted an appreciable reduction in the necessary amount of ascorbic acid.

While sulfur dioxide was the most effective agent used in preventing browning an examination of the flavor scores in Tables I and II shows that the sulfur dioxide treatment adversely affected the flavor. If a lower and safer concentration had been used to prevent the adverse flavor effect, its advantage over ascorbic acid in preventing discoloration would probably have been less marked.

Calcium Salts as Firming Agents

Sliced apples preserved by freezing for pie-making often undergo an undesirable amount of fragmentation and disintegration during the process. This is especially true of soft-fleshed varieties and becomes increasingly noticeable in many varieties as the flesh becomes softer.

The use of calcium salts to reduce softening in tomatoes during processing is common. It has been used beneficially on other crops where an undesirable amount of breaking up or disintegration occurs.

The use of calcium salts with apples in the present studies gave generally disappointing results. Fruit packed at a pressure test of 12 pounds or above usually retained its shape satisfactorily during freezing and cooking without further treatment. Fruit slightly softer than this, having readings between 9 and 11 pounds, showed some beneficial

Table IV *(continued)*

Variety	*Source*	*Pack No.*	*Pressure Test, Lb.*	*Control Untreated*	*Potassium Metabisulfite*[b]	*Ascorbic Acid*[c]	*Citric Acid*[d]	*Ascorbic and Citric Acids*[e]
Lowry	Va.	1	16.7	8.7	2.9	2.7	2.6	2.6
		2	11.5	5.3	2.0	1.8	2.8	1.7
		3	10.0	6.4	2.6	3.4	4.1	1.7
		4	8.4	3.7	1.5	1.7	3.0	1.7
McIntosh	N. Y.	1	11.0	5.0	2.8	3.2	3.7	2.5
		2	8.8	5.0	2.0	2.8	3.6	2.8
		3	7.4	5.9	2.2	2.8	5.2	3.2
		4	7.0	4.2	1.5	2.7	3.9	2.7
Northern Spy	Mich.	1	14.3	4.8	1.9	3.7	3.9	3.6
		2	11.9	4.6	3.3	3.4	3.3	3.0
		3	11.3	5.3	2.2	3.9	4.5	3.1
		4	9.5	5.5	2.5	3.0	4.2	3.0
Northern Spy	N. Y.	1	14.9	4.1	2.1	2.2	3.3	2.5
		2	11.8	3.8	1.4	3.0	3.2	3.0
		3	9.8	3.3	2.4	2.9	4.0	2.3
		4	9.5	5.0	1.5	1.7	3.5	1.7
Rhode Island	N. Y.	1	12.9	6.4	2.5	3.7	5.7	3.5
		2	10.2	6.2	2.1	3.4	3.0	3.5
		3	9.5	5.0	2.1	2.2	2.9	3.3
		4	8.7	5.1	1.7	3.0	3.5	3.1
Rome Beauty	Md.	1	16.5	5.8	1.9	2.7	2.7	2.8
		2	12.7	5.1	1.8	1.5	3.4	3.0
		3	11.8	4.5	1.1	2.2	2.6	2.0
		4	10.6	3.0	1.2	1.2	1.6	2.0
Stayman Winesap	Md.	1	16.4	4.5	1.8	2.7	3.5	2.1
		2	10.5	4.1	1.3	1.9	3.0	1.6
		3	8.5	4.6	2.0	2.8	2.5	1.7
		4	7.8	3.7	1.2	1.7	2.2	1.7
Turley	Ohio	1	10.2	3.6	2.3	3.0	4.0	2.0
		2	8.7	3.5	1.8	2.5	3.3	2.5
		3	8.5	4.3	2.8	4.2	5.6	3.0
Winesap	Va.	1	17.3	2.7	2.4	2.3	2.3	2.7
		2	13.0	3.0	1.8	1.6	3.0	1.3
		3	10.3	3.4	2.8	2.6	2.6	3.0
		4	9.7	2.5	1.6	2.7	2.3	2.5
Yellow Newtown	Md.	1	17.4	2.4	1.0	1.8	1.5	2.4
		2	16.4	2.5	1.3	1.6	1.6	1.6
		3	15.0	2.5	1.6	2.1	2.1	2.9
		4	13.6	3.6	1.7	1.6	2.5	1.6
		5	13.5	3.5	1.3	1.6	2.7	3.5
York Imperial	Md.	1	16.3	5.1	3.6	4.6	4.7	2.6
		2	15.4	4.5	1.3	1.8	3.3	2.0
		3	13.3	3.3	1.9	2.1	2.8	2.6
		4	12.0	4.0	1.2	2.0	2.2	2.0
		5	10.9	4.3	...	1.9	3.0	...
		6	10.4	3.2	1.1	2.3	4.0	...
Average all lots				4.00	1.96	2.43	3.10	2.36

[a] Mean scores. 1 to 1.9, excellent; 2 to 3.5, very good to good; 3.6 to 4.9, fair to poor; 5 to 6, barely or doubtfully acceptable; above 6, unacceptable.

[b] Packs 1 and 2 dipped for 1 minute in a potassium metabisulfite solution containing 1500 p.p.m. of sulfur dioxide; later packs dipped for 2 minutes in solution containing 1000 p.p.m.

[c] Ascorbic acid dissolved in sirup to give a concentration of 1 part of acid to 2500 parts of fruit and sirup.

[d] Citric acid dissolved in sirup to give concentration of 1 part of acid to 1000 parts of fruit and sirup.

[e] Ascorbic and citric acids dissolved in sirup to give concentration of 1 part to 2500 and 1 part to 1000 parts, respectively, of fruit and sirup.

effects if the sliced fruit were dipped in a 0.1 to 0.2% solution of calcium chloride for 5 to 10 minutes. If the fruit had readings below 9 pounds, this treatment was progressively less effective and higher concentrations or longer periods of immersion adversely affected the flavor.

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VEGETABLE OIL STABILIZATION

Preparation and Evaluation of Two New Fat-Soluble Metal Inactivators

A. W. SCHWAB and C. D. EVANS
Northern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Ill.

Two new fat-soluble metal inactivators have been prepared and evaluated for stabilization of vegetable oils. One of the compounds, a mono-octadecyl ester of (carboxymethylmercapto)-succinic acid, is of the tridentate type, having two carboxy groups in either α or β positions to the coordinating sulfur atom. The other, a mono-octadecyl ester of thiodisuccinic acid, belongs to the tetradentate class. Both compounds have the essential structure for effective chelation of metals. The tetradentate compound was not superior to the tridentate compound in stabilizing soybean oil against oxidative deterioration. The mono-octadecyl ester of (carboxymethylmercapto)-succinic acid represents a new type of ester of this acid. It did not impart an objectionable flavor to soybean oil and good solubility in oil was attained. The heat instability of the ester will limit its addition to the cooling phase of the deodorization. Good oxidative stabilities were obtained for the mono-octadecyl ester of thiodisuccinic acid in the usual concentration range employed for inhibitors. A significant improvement in the organoleptic flavor scores of the treated samples over that of the control was noted in both initial and aged samples. Again the disadvantage of heat instability limited the addition of the ester to the cooling phase of the deodorization.

Soybean oil is subject to deterioration by catalytic effects of pro-oxidant metals, such as iron and copper. A number of compounds, known as metal inactivators, have been and are being added to the edible oils to destroy the catalytic effects of these metals. At present the edible-oil industry lacks a metal-chelating agent which is nontoxic, does not impart undesirable odor, flavor, or color, and is heat-stable, readily available, and oil-soluble. The present investigation was undertaken in an effort to develop a fat-soluble metal inactivator more effective and satisfactory than any previously described.

Sulfur compounds of the tridentate class having two carboxy groups in either α or β positions to the coordinating atom have been found very effective in stabilizing vegetable oils (*7*). Recently (carboxymethylmercapto)-succinic acid has been shown to possess high activity (*7*). This acid has two carboxy groups α to the sulfur atom and one carboxy group in the β position. Actually, the molecule has one more carboxy group than is necessary for complexing the iron. It should be possible to prepare an alkyl ester of this extra group with a long-chain fatty alcohol which might impart solubility in oil. However, it is important to esterify the proper carboxyl, so as not to lose the arrangement which permits the formation of chelate rings and the complexing of iron in an octahedral configuration.

Three types of esters of (carboxymethylmercapto)-succinic acid have been prepared by Mulvaney, Murphy, and Evans (*5*). Mattano and Hixon (*3*) have been granted a patent on the rust-preventing action of these esters in turbine oils. These workers used either an ester of mercaptoacetic acid or a diester of maleic acid in their preparations. None of these combinations gives the best configuration for effective metal chelation. By employing mercaptoacetic acid and a monoester of maleic acid, a more desirable molecule is obtained, containing symmetrical carboxy groups in either α-α or α-β positions to

Table I. Heat Stability of Mono-octadecyl Esters of (Carboxymethylmercapto)-succinic Acid and Thiodisuccinic Acid

Ester, 0.01% Concn.	Peroxide Values, 8 Hours A.O.M.	Oxidative Index[a]	Heat Stability
MECSA added before deodorization	65	1.1	Unstable
Control A	72		
METSA added before deodorization	30	1.2	Unstable
Control B	37		
MECSA added after deodorization	9.5	5.7	Stable
Control A	54		
METSA added after deodorization	6.0	5.5	Stable
Control B	33		

[a] Ratio of peroxide value of control to peroxide value of oil-containing inactivator.