

## Nitrate-Induced Corrosion of Tin Plate as Affected by Organic Acid Food Components

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The accelerating effect of nitrates on the dissolution of tin observed in tin plate cans of acid products has been investigated through canned model packs experiments. The relative contribution to the tin dissolution of three typical organic acid food solutions (at a total of 1% acid concentration), citric acid, malic acid, and their mixture with oxalic acid, found naturally as a complexing system in fruits and juices having a pH of 3.5, has been explored. The behavior of three levels of nitrate, 50, 125, and 250 ppm, was compared in pure acid solutions and in acid solutions with 15% added sucrose. The effectiveness of the addition of 500 ppm of ascorbic acid in inhibiting this type of corrosion was tested. The decrease in the nitrate concentration and the increase in the concentration of tin and iron were followed in the canned model solutions throughout suitable storage periods at room temperature. The order of the corrosion rates in the pure acid solutions was: the mixture of acids > citric acid ≥ malic acid. The addition of sucrose and sucrose-ascorbic acid to the acid solutions reduced the rate of tin dissolution in the mixture of acids and in malic acid, but had no effect in citric acid solutions.

Studies on the accelerated corrosion reaction of plain tin plate cans filled with nitrate-containing acid foods have received considerable emphasis (Strodtz and Henry, 1954; Horio et al., 1964/65, 1966, 1968; Farrow, 1970; Farrow et al., 1969-1971; Evans, 1971; Saguy et al., 1973; Semel and Saguy, 1974) in the last 20 years, reflecting its world-wide occurrence. The incidence has increased since the problem was first reported, with nitrate suggested as the most probable cause of this phenomenon.

Due to the seriousness of the economic consequences of this problem much experimental work has been carried out on the reaction of nitrate-containing acid foods with tin plate in an effort to define the mechanism of the reaction and to find a way to inhibit it. However, little information is known about the manner in which nitrate induces corrosion in the specific citrus fruit media.

The presence of nitrate in canned foods alters the chemical reaction involved in the common form of slow detinning that occurs in most plain cans. Data in the literature (Strodtz and Henry, 1954; Horio et al., 1964/65, 1968; Board and Elbourne, 1965; Farrow et al., 1969; Board, 1973) on the mechanism of nitrate-induced accelerated detinning corrosion suggested that it affects the cathodic part of the corrosion process, which is normally rate determining. Nitrate acts as an electron acceptor for the electrons produced when tin dissolves. The hydrogen evolution reaction is replaced by the electron-nitrate two-step reduction reaction, which can take place on the large tin electrode; then the rate of detinning depends on the concentration of nitrate and the concentration of H<sup>+</sup> ions or the pH. It has been shown that the first reduction step, the reduction of nitrate to nitrite, is a slow reaction, and presumably rate determining, but reduction of nitrite to the ultimate reduction product—ammonia—is fast (Horio et al., 1964/65). It was also shown that nitrate does not immediately affect the corrosion rate, but begins to act after tin (Horio et al., 1968) or iron (Thomas et al., 1966) ions have passed into solution (Sherlock et al., 1972). Oxygen present in the can at the time of processing triggers the nitrate-detinning reaction by increasing the initial rate

of formation of Sn<sup>2+</sup> (Horio et al., 1968).

The mechanism of the reaction may be affected by the chemical composition of a specific food. Components that may affect it are most probably the organic acids—as judged by the pH effect—due to their H<sup>+</sup> concentration, or by their ability to bind free stannous or ferrous ions, resulting from interaction between the tin plate container and food, in stable chelates, particularly at the low pH values (3.5, 4) commonly encountered in citrus foods (Nehring, 1966; Mahadevaiah et al., 1969; Willey, 1972; Gruenwedel and Hao, 1973).

Previous work has shown that the effect of nitrate is pH dependent (Strodtz and Henry, 1954; Thomas et al., 1966; Board and Holland, 1969); raising the pH above 6.0 effectively inhibits nitrate detinning of tin plate cans, but this procedure cannot be used with acid foods where the acidity determines the organoleptic properties and the heat-treatment requirements, e.g. tomato or citrus fruit products. Board and Holland (1969) obtained inhibition of the nitrate-induced corrosion reaction in some products which contained particular sulfur compounds.

As a preliminary to a search for alternative inhibitors, information on the organic acid make-up and on the content of oxidizing or reducing substances will elucidate the nitrate-induced corrosion mechanism in particular food systems.

The present experiment was designed to determine how the main organic acid components in citrus fruit juices affect the nitrate-induced corrosion reaction at the pH (3.5) usually found in canned citrus products. Model solutions simulating citrus fruit juices of citric and malic acids and a mixture of these with oxalic acid were prepared and used to follow the nitrate-induced corrosion reaction at a low pH.

### EXPERIMENTAL SECTION

**Materials.** Plain cans for test-pack experiments were manufactured by the Israel Can Company from a single batch of electrolytic tin plate. Measurements on the interior of unfilled cans showed a free-tin coating weight of 0.82 lb/ base box (bb) an alloy-tin coating weight of 0.12 lb/bb, and an ATC value of 0.11  $\mu\text{A}/\text{cm}^2$  (means of six determinations). Can ends were also made from a single batch of plain electrolytic tin plate. Throughout the experiments 202 × 202 cans (100 g), as described above, were used.

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Table I. Composition of pH 3.5 Model Solutions

Organic acids, %			NO <sub>3</sub> <sup>-</sup> level, ppm	Additives	
Citric	Malic	Oxalic		Su-crose, %	Ascorbic acid, ppm
1					
1			50		
1			125		
1			250		
1				15	
1			50	15	
1			125	15	
1			250	15	
1			125	15	500
	1				
	1		50		
	1		125		
	1		250		
	1			15	
	1		50	15	
	1		125	15	
	1		250	15	
	1		125	15	500
0.8	0.1	0.1			
0.8	0.1	0.1	50		
0.8	0.1	0.1	125		
0.8	0.1	0.1	250		
0.8	0.1	0.1		15	
0.8	0.1	0.1	50	15	
0.8	0.1	0.1	125	15	
0.8	0.1	0.1	250	15	
0.8	0.1	0.1	125	15	500

All solutions were prepared from reagent-grade chemicals and deionized water (<0.22 ppm of NO<sub>3</sub><sup>-</sup>). Stock model solutions were prepared by dissolving weighed amounts ( $\pm 0.1$  mg) of sucrose, citric acid, malic acid, oxalic acid, ascorbic acid, and sodium nitrate in the volume required, with a pH adjustment before making up to the mark with deionized water. Table I gives the exact compositions of the model solutions used. Control packs lacking nitrate were prepared similarly.

**Methods.** Nitrite and nitrate were determined by the method previously described by Green (1970) and Fudge and Truman (1973). The same method has been developed for use with the Technicon Auto-Analyzer (Henriksen and Selmer-Olsen, 1970). The minimum detectable amounts were  $0.05 \pm 0.02$  ppm of nitrate and  $0.03 \pm 0.02$  ppm of nitrite.

Tin and iron were determined by atomic absorption analysis performed on a Pye-Unicam, Model SP-90 atomic absorption spectrometer using an air-acetylene flame. The minimum detectable amount of tin was  $25 \pm 5$  ppm (measured at 286.3 nm) and that of iron was  $1 \pm 0.1$  ppm (measured at 248.3 nm).

Tin-coating thickness was determined by the coulometric method of Kunze and Willey (1952), the constant stripping current being supplied by an Elron Galvanostat, Model CHG-1. A plexiglass vessel with a sample holder, ensuring a constant area of 6.6 cm<sup>2</sup> (the anode) and a stainless steel (reference cathode) electrode containing 1 N HCl solution, constituted the electrolysis cell. Recordings of the time-potential curves were made by a Telrad Model 822-918 variable-speed recording potentiometer. Measurements were taken directly from the record charts and converted to coating weights by the use of the Faraday equivalent for tin (0.615 mg/C) and the calculated value of 0.507 mg/C for the alloy.

All ATC value determinations were made by a standard instrument constructed in accordance with ASTM A623 (1973).

**Procedure.** Cans were filled with model solutions in

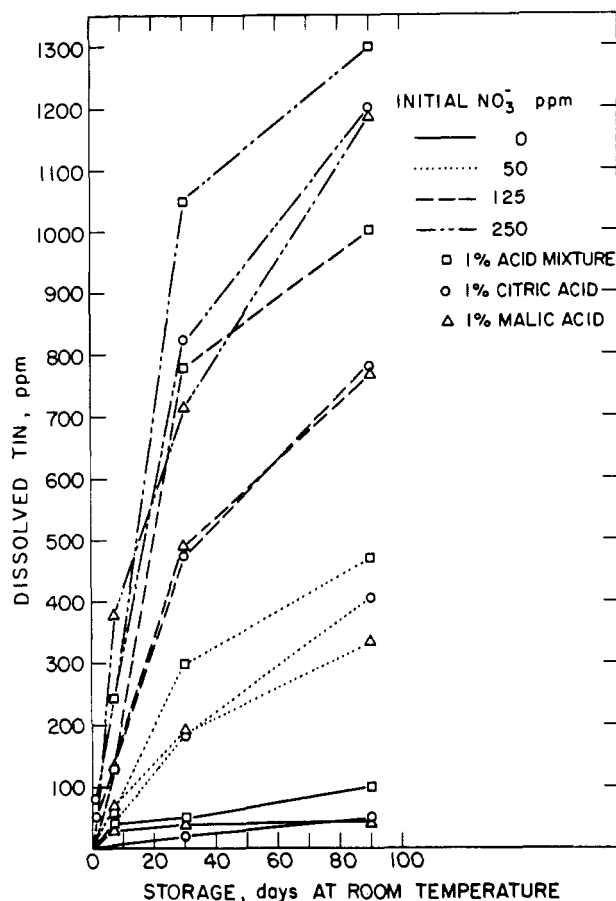


Figure 1. The effect of organic acid solutions (pH 3.5) at three NO<sub>3</sub><sup>-</sup> levels on tin plate tin dissolution as a function of storage.

accordance with commercial canning practice for acid products: solutions were heated to 90 °C, poured into cans (filled, with minimum head space), closed, and processed in water at 82–85 °C for 10 min. Cans were cooled immediately and stored at room temperature.

Samples of each model solution were taken from storage (at room temperature) at 1, 7, 30, 90, and 180 days, for determination of dissolved tin and iron, total nitrate, nitrite, and sucrose, and pH. Vacuum was determined before each opening. The presence or absence of corrosion was noted after opening and the residual, internal tin-coating weight was determined by the coulometric method. All the experiments were conducted in two replicates.

#### RESULTS AND DISCUSSION

The separate effects of citric acid, malic acid, and a mixture of citric, malic, and oxalic acids at three nitrate levels (50, 125, and 250 ppm) on tin dissolution were followed in model solutions of 1% total acid concentration at pH 3.5. Results are shown in Figures 1 and 2. Results are expressed as parts per million of tin dissolved in the model solutions as a function of length of storage at room temperature. The shape of the curves obtained for the three levels of nitrate used showed an initial rapid detinning reaction up to 1 month, followed by a slower rate during longer storage. The similar amounts of dissolved tin found in cans containing citric or malic acids reflect similar rates of tin corrosion, while the greater amounts of dissolved tin found in cans containing 0.1% oxalic acid in a total 1% mixture of citric and malic acids suggest greater rapidity of corrosion.

The nitrate concentration in cans decreased at the expected rates, and corresponded with the rate of tin dissolution. Figure 2 shows the decrease in nitrate con-

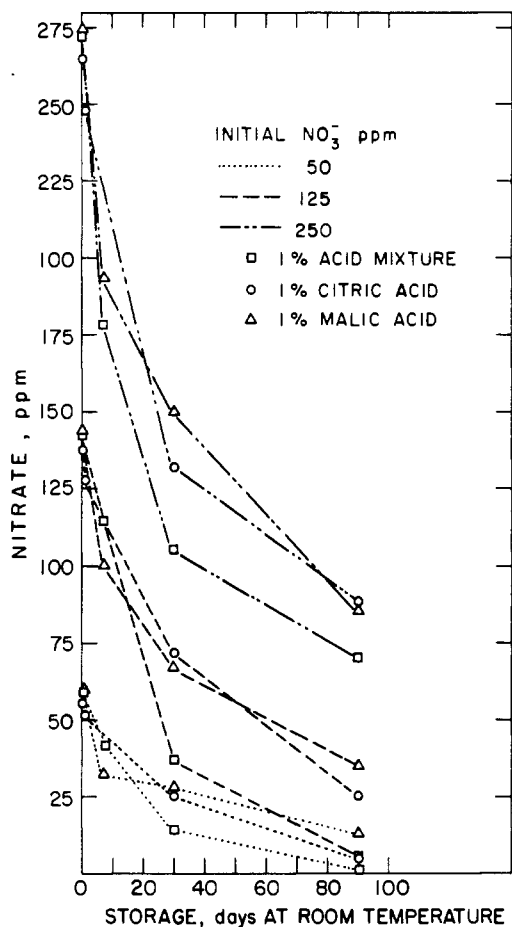


Figure 2. Decrease of  $\text{NO}_3^-$  concentration during detinning in organic acid solutions (pH 3.5) at three  $\text{NO}_3^-$  levels as a function of storage.

centration during storage at room temperature in model acid solutions with initial nitrate levels of 50, 125, and 250 ppm.

The results of measurements of the tin corrosion rate and hence the rate of reduction of nitrate in solutions containing 1% citric acid, 1% malic acid, and the mixture of total 1% acids (0.8% citric acid, 0.1% malic acid, and 0.1% oxalic acid) at pH 3.5 and nitrate contents of 50, 100, and 250 ppm, indicate the order in which the corrosion rates for the acid solutions tested fall: the mixture of the acids  $>$  citric acid  $\geq$  malic acid. At 50 and 125 ppm initial nitrate levels, differences between corrosion rate are more marked, e.g., 470, 420, and 330 ppm, and 980, 780, and 760 ppm of dissolved tin, respectively, over a 90-days storage period. At the 250-ppm nitrate level there were no marked differences in these values.

The effect of sucrose addition on the nitrate-induced corrosion reaction of tin plate in solutions of 1% total acids was also investigated. It was observed that a 15% sucrose concentration had little or no effect on the rate of tin dissolution in malic or citric acids, if compared with rates obtained in acid solutions without sucrose addition, but had a greater effect in solutions containing oxalic acid (Figure 3). At 125 ppm of  $\text{NO}_3^-$  initial level, the addition of 15% sucrose to the solution containing the mixture of the acids reduced the amount of dissolved tin in cans after 90 days of storage from 980 to 760 ppm; at a 50-ppm nitrate initial level, the amount of dissolved tin fell from 470 to 370 ppm. The same behavior was observed in the decrease of nitrate concentration during the storage of cans at room temperature when 15% sucrose was added to the model solutions containing citric acid, malic acid, or the

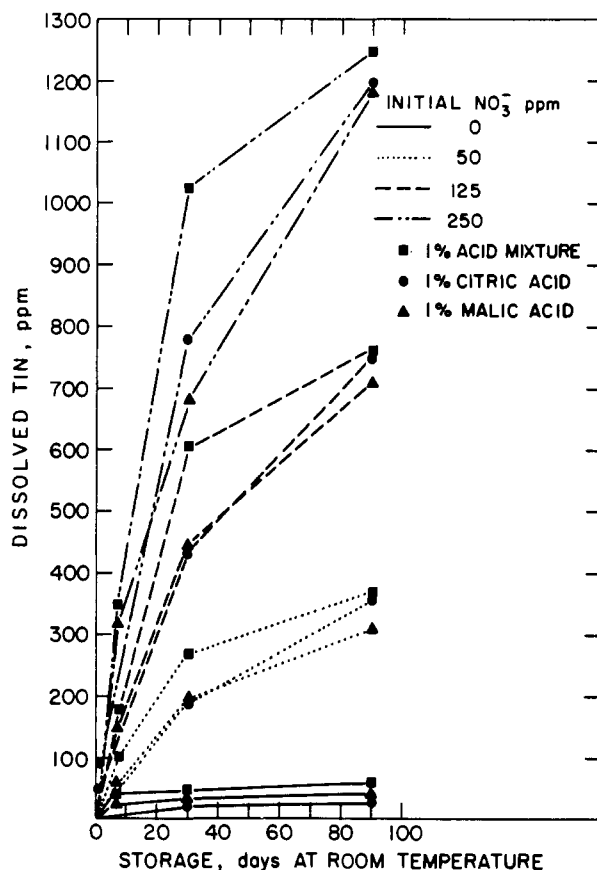


Figure 3. The effect of organic acid solutions (pH 3.5) at three  $\text{NO}_3^-$  levels containing 15% sucrose on tin plate tin dissolution as a function of storage.

acid mixture also containing oxalic acid (Figure 4).

The presence of ascorbic acid in acid model solutions was also studied with regard to the tin dissolution in the  $\text{NO}_3^-$  presence. Ascorbic acid is one of the fruit juice components, and is most commonly encountered at levels of 10–1000 ppm. By its oxidation–reduction properties it may act as a natural component reducing the contribution of nitrate to the corrosion of tin. The effect of 500 ppm of ascorbic acid added to 1% total acid model solutions and 15% sucrose at 125-ppm initial nitrate level in cans stored at room temperature was followed. The values of the dissolved tin during a 90-day storage period are presented in Figure 5. A comparison with control solutions (without ascorbic acid) showed that the ascorbic acid did not affect tin dissolution in citric acid solution, but that corrosion was reduced in the 1% malic acid and the 1% citric–malic–oxalic acid mixture with 15% added sucrose. The rate of nitrate decrease concentration showed the same pattern (Figure 6). From this behavior it may be concluded that the ascorbic acid partly inhibited detinning in model solutions of 1% malic acid and the 1% mixture of citric–malic–oxalic acids, but had a negligible effect on the rate of detinning by the nitrate in the 1% citric acid solution.

Nitrite was not detected in any of the cans, a result consistent with reports (Board, 1973) that nitrite reduction is rapid. The vacuum in the cans did not change appreciably during storage. The quantity of dissolved iron at nitrate levels less than 250 ppm varied from 1 to 3 ppm for the entire 3-month storage period, showing that at nitrate concentrations up to 125 ppm, acid solutions dissolve mainly tin. There were marked variations among the three solutions containing 250 ppm of nitrate, during the same storage period (Figure 7). The 1% malic acid

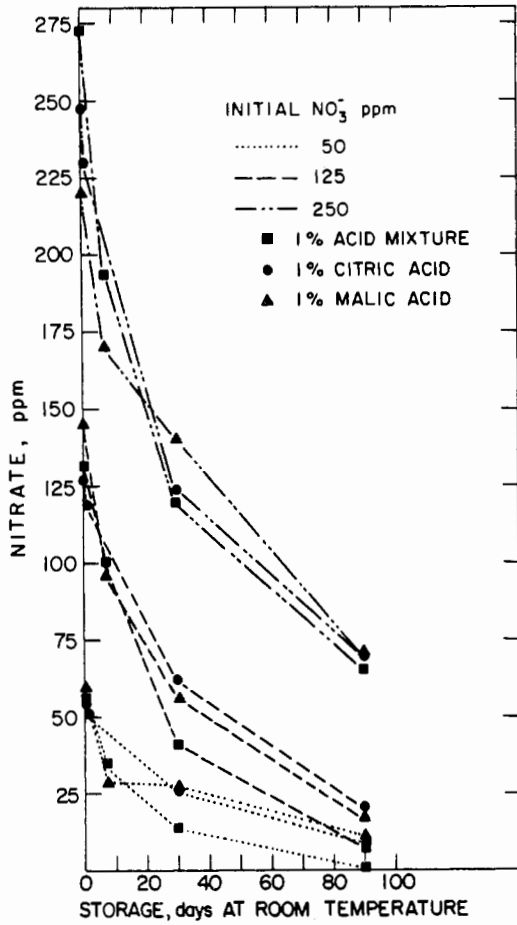


Figure 4. Decrease of NO<sub>3</sub><sup>-</sup> concentration during detinning in organic acid solutions (pH 3.5) at three NO<sub>3</sub><sup>-</sup> levels, and containing 15% sucrose, as a function of storage.

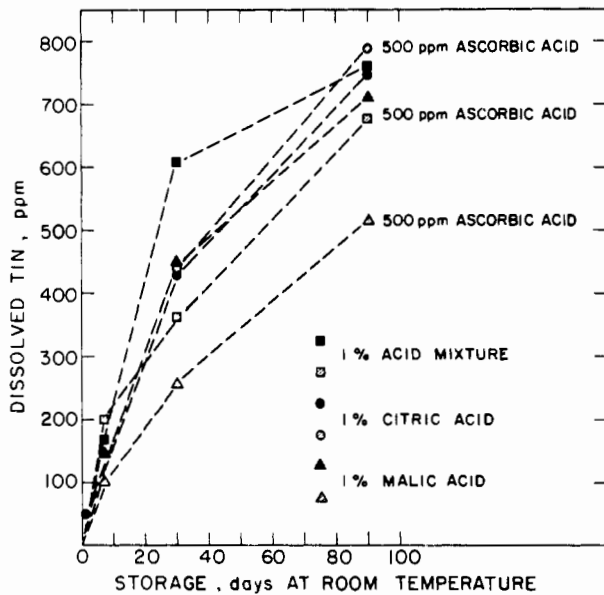


Figure 5. The effect of 500 ppm of ascorbic acid in organic acid solutions (pH 3.5) at 125 ppm of NO<sub>3</sub><sup>-</sup> and containing 15% sucrose, on tin plate tin dissolution, as a function of storage.

solution had the least dissolved iron (2 ppm), even after 3 months, when the cans were almost detinned. Cans with the 1% citric-malic-oxalic acid mixture showed iron corroding at an appreciable rate: 22 ppm of iron dissolved in the same 3-month period. The addition of 15% sucrose to the acid solutions had some effect in reducing iron

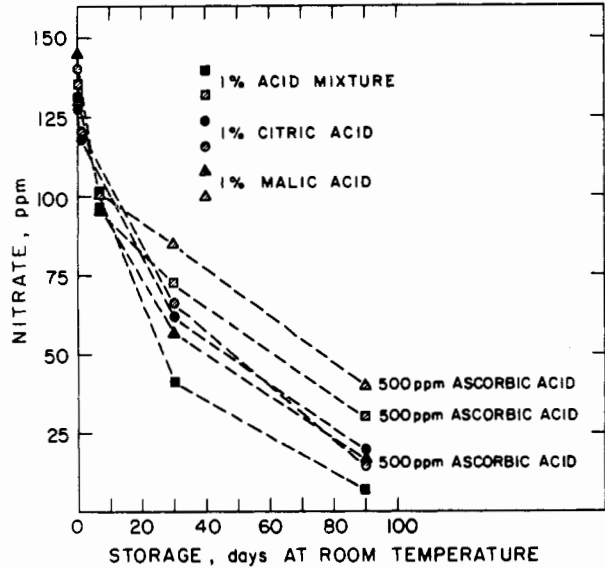


Figure 6. Decrease of NO<sub>3</sub><sup>-</sup> from an initial 125-ppm level during detinning in organic acid solutions (pH 3.5), containing 15% sucrose plus 500 ppm of ascorbic acid, as a function of storage.

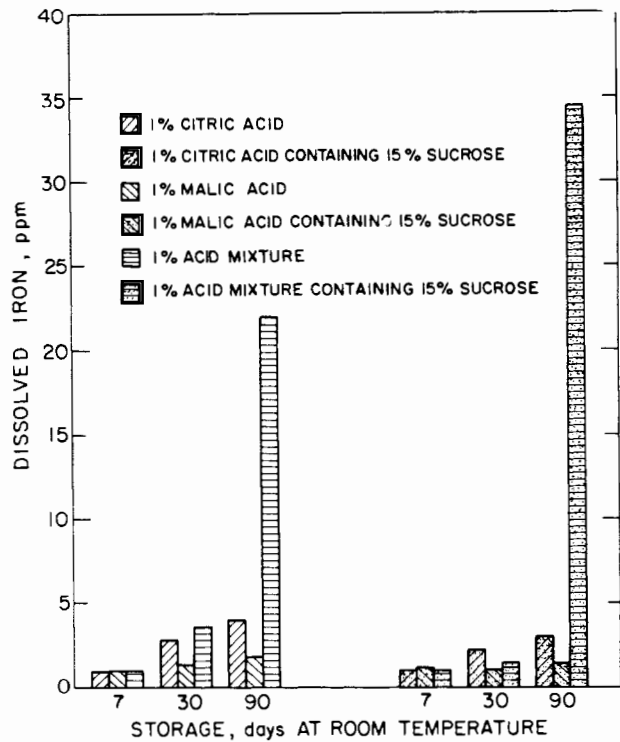


Figure 7. The effect of organic acid solutions (pH 3.5) at 250 ppm of NO<sub>3</sub><sup>-</sup> with or without the addition of 15% sucrose, on iron dissolution, as a function of storage.

dissolution in cans of 1% malic acid or 1% citric acid at the three nitrate levels tested (from ~4 ppm to ~2 ppm), as well as in cans containing the 1% acid mixture of citric-malic-oxalic acids and at 50- or 125-ppm NO<sub>3</sub><sup>-</sup> initial level. However, in cans containing this acid mixture and at a 250-ppm NO<sub>3</sub><sup>-</sup> initial level, the amount of dissolved iron was even higher, 35 ppm.

Ascorbic acid at the 500-ppm level showed no effect on iron dissolution in cans as compared with the 15% sucrose + 1% citric acid solution at pH 3.5 containing 125 ppm of NO<sub>3</sub><sup>-</sup>. But 500 ppm of ascorbic acid added to the 1% malic acid-sucrose solution or to the 1% acid mixture-sucrose solution showed an increasing amount of iron

dissolved upon 90 days of storage at the same nitrate concentration.

The internal appearance of the cans was also examined. Control packs generally showed a gradual increase in tin-etch during storage, but no detinning. Cans with added nitrates showed progressive detinning, up to complete detinning in those with 250 ppm of nitrate.

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## Polymetaphosphate and Oxalate Extraction of Sunflower Pectins

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The potential of sunflower heads as a commercial source of low methoxyl pectin was investigated using two solvent systems over a range of temperature, concentration, and pH. By raising the temperature of extraction from 60 to 90°C, the yields of oxalate- and Calgon-extracted pectins were increased from 9 to 17% and from 15 to 20%, respectively. Although the high temperatures adversely affected anhydrouronic acid and methoxyl group contents of oxalate-extracted pectins, the levels of these constituents exceeded those of Calgon-extracted pectin at each temperature level. Increasing the concentration of Calgon improved the pectin yields but there was a proportionate increase in ash content of the pectin and even lower anhydrouronic acid and methoxyl group levels were obtained. Sodium hexametaphosphate was a more efficient solvent than Calgon but ash level in the dried pectin was still 8% even after rewashing with acidic alcohol, and the gel power was only 39.0. Residual ash levels in the oxalate-extracted pectin were reduced to 2% by acidic alcohol washing and the gel power values averaged 118. High ash levels appeared to adversely affect the gel power of the pectin and improved methods for removal of polyphosphate are needed if the latter solvent is to be used for commercial sunflower pectin extraction.

Despite the high pectin content of sunflower heads, the commercial production of sunflower pectin has not been undertaken because of problems associated with extraction. Shewfelt and Worthington (1953) demonstrated that oxalic acid-ammonium oxalate was superior to hydrochloric acid or sodium polyphosphates in the extraction of pectin from sunflower heads. Hot dilute solutions of ammonium oxalate-oxalic acid were also used successfully for the

extraction of pectin from polysaccharides in sunflower heads by other workers (Bishop, 1955; Riaz and Uddin, 1972), and also in this laboratory (Sabir et al., 1975). However, ammonium oxalate-oxalic acid forms calcium oxalate in isolated pectin and the complex can only be removed by extensive washing with acidified alcohol at a low pH. The acid treatments would have adverse effects on pectin quality and the problem of oxalate residues in the final product has not been resolved.

Polyphosphates are widely used as solvents in the food industry and some workers have utilized polyphosphates for the extraction of pectin from other plant tissues than sunflower (Baker and Woodmansee, 1944; Maclay and Nielsen, 1945). Polyphosphate-calcium complexes are highly soluble in aqueous ethanol at low pH and, therefore,

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