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CORROSION IN FOOD CONTAINERS

The Mechanism of Corrosion of Tin Plate by Various Food Products

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The corrosion mechanism of tin plate under conditions duplicating normal canned-food packs was studied. In grapefruit and tomato juice, the dissolution of the tin coating is accompanied by the evolution of hydrogen; in prunes, hydrogen does not appear to be evolved when the tin dissolves, but only when the steel base is attacked. In prunes, all tin plates detin at the same rate, but in grapefruit and tomato juice the rate of detinning is not the same for different types of tin plate. Electrochemical data indicate the presence of depolarizers in prunes, but not in grapefruit juice, a fact that explains the different corrosion mechanisms in the various food products.

THE CORROSION MECHANISM of tin plate by various food products has been the subject of extensive investigations by the steel industry and the can-manufacturing industry. In the late 1920's, various groups showed that in deoxygenated acid-food products, tin is anodic to the steel base and protects it at its own expense (4-6). The next 15 years were spent primarily in investigating the effect of different manufacturing variables on the corrosion performance of tin plate (2). In recent years, work has been directed toward a study of the corrosion mechanism and the interrelation of the three reactions that occur in the corrosion process: dissolution of the tin, dissolution of the steel base, and evolution of hydrogen (1, 3, 7). Most of this work has been performed with prunes in water as an accelerated corrosion medium.

The purpose of the research reported was to determine whether the corrosion mechanism of tin plate is the same in all food products as in prunes.

Experimental

The three food products used as corrosive media were prunes in water, grapefruit juice, and tomato juice. They were packed in No. 2 (307 × 409) cans, made from 0.50 pound per base box (a trade unit; 1 pound per base box equals 454 grams of tin per 201,272 sq. cm. of steel surface) tin plate according to normal canning procedures, and then stored at 37.8° C. Therefore, except for the high temperature storage, this pack simulated a normal commercial pack. The volume of the corrodant was approximately 570 ml., and the surface area exposed to it was approximately 310 sq. cm. This area was covered with a layer of tin 0.65 micron thick. This quantity of

tin is equal to 2.5 meq. of stannous tin per can. Between the tin and the steel base was an iron-tin compound, FeSn₂, that was approximately 0.15 micron thick.

To follow the corrosion kinetics, data were obtained for tin and iron dissolution and hydrogen evolution as a function of time. Because data on the tin and iron contents of the food products could be obtained only by destructive methods, a group of cans was set aside specifically for that purpose. Three to five cans were opened at predetermined intervals and the contents were analyzed for tin and iron. The results were expressed in terms of milliequivalents of stannous tin and ferrous iron. The rate of change of hydrogen content was determined by observing the change in the contour of the can end. The ends of a can behave like a diaphragm, in that they deflect with change in internal pressure. A micrometer dial-depth gage permits measurement of this deflection, the double seam being used as a reference. The relationship between the change in the deflection and the change in the pressure in the can is shown in Figure 1.

The data obtained for the hydrogen pressure in the above manner were

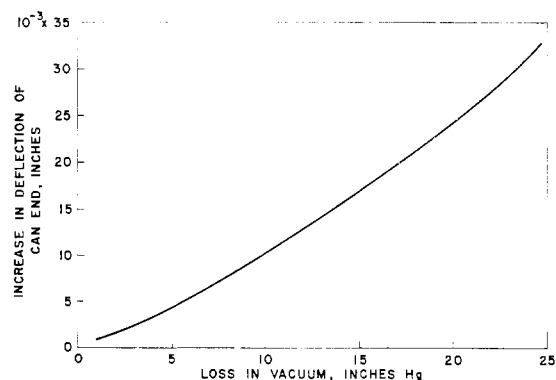


Figure 1. Change in dial reading vs. change in internal pressure

converted to milliequivalents of hydrogen by using the ideal gas law and assuming that the head space of the cans averaged 40 ml. This is an average value for commercially packed cans and can vary over wide limits, inasmuch as 1 mm. of head space is equivalent to 6.3 ml. of volume.

The calculation of the evolved hydrogen contained numerous assumptions, —e.g., all the evolved gas was hydrogen; none of the hydrogen dissolved in the corroding solution, food product, or steel base or diffused through the can.

With respect to the first assumption, analyses of the head space gas indicate that some carbon dioxide is also given off, but the quantity is small compared to the quantity of evolved hydrogen. The last two assumptions are also not completely valid. The resultant error, however, is in the direction opposite to that of the first assumption, so that the errors tend to cancel. Furthermore, the results, if not quantitative, show very definite qualitative trends.

Results and Discussion

The milliequivalents of the three corrosion products are plotted as a function of time for the corrosion of one

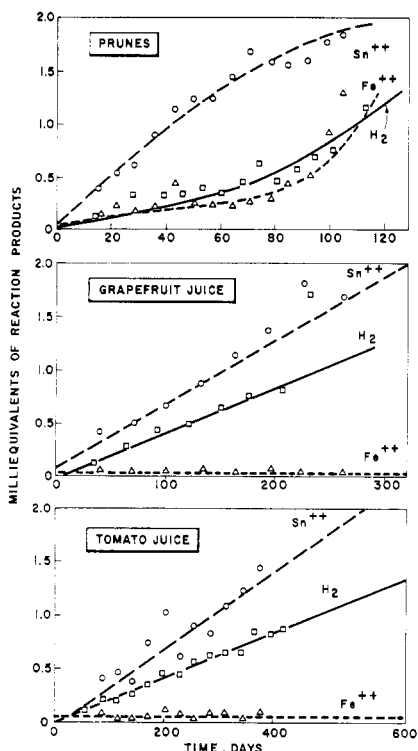


Figure 2. Reaction products for corrosion of tin plate in juices

lot of tin plate in prunes (Figure 2). Similar curves were observed for four other lots of tin plate. These data confirm earlier work (1, 3-7). Specifically, they show that hydrogen does not appear to be evolved as the tin corrodes, but is given off only when the iron is attacked. This point would be even more apparent for tin plate with a thicker tin coating, as the hydrogen and iron curves would be horizontal for a period of time, while the tin dissolved and would begin to rise only when insufficient tin remained on the can body to afford protection to the steel base.

Figure 2 also shows similar plots for the corrosion of tin plate in grapefruit and tomato juice. The same lot of tin plate that had been used for the prune packs was used for these experiments. Similar plots were obtained with numerous other lots of tin plate. In these cases, hydrogen is evolved as the tin dissolves, in contrast to the reverse situation with prunes. For grapefruit juice, the data correspond to observed performance, inasmuch as cans that show complete vacuum loss usually have relatively little iron dissolved in the product, compared with that present in similar cans packed with prunes. Comparable information on tomato juice packs is not available at present. Whether the differences between the tin and the hydrogen curves for grapefruit juice and tomato juice in Figure 2 are real is not known. The assumptions made in the calculation of the hydrogen tend to give low results and could account for the difference.

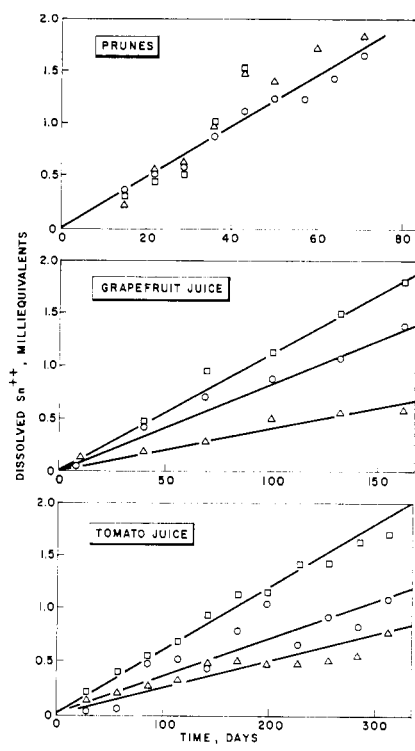


Figure 3. Tin dissolution curves for various tin plates in juices

Vaurio (7) has stated, "for a given lot of prunes, the average rate of solution of tin at 100° F. (37.8° C.) is constant with time irrespective of the thickness of the tin coating, the type of tin deposit, or the corrosion-resistant quality of the steel base." Tests on numerous lots of tin plate show this to be true for the corrosion of tin plate in prunes (Figure 3, the different symbols representing different tin plates). However, the data do not show this to be true for grapefruit and tomato juice (Figure 3). Instead, the rate of tin solution is a function of the particular lot of tin plate under examination.

The above data show that the corrosion mechanism of tin plate is a function of the food product in which the tin plate is corroding, and that the results cannot be extrapolated from one corroding medium to another.

The difference in the corrosion mechanism of tin plate from one food product to another must be accounted for. It has been theorized that there is a cathodic depolarizer present in prunes—a substance that can oxidize tin more readily than can the hydronium ion. If this is true, one should be able to detect it with any of the numerous electroanalytical techniques available today. Conversely, no such depolarizer should be present in grapefruit and tomato juice.

Polarography was chosen as the most convenient means of verifying this. The juices were filtered to remove all solid particles that might adsorb on the electrode surface and distort the current-voltage curves. Polarograms were obtained on the filtered juices at a drop-

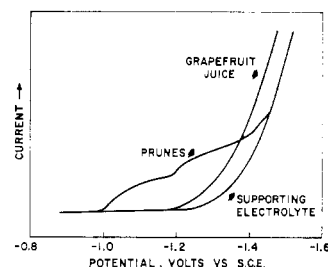


Figure 4. Polarograms of prune juice and grapefruit juices in a citrate buffer at dropping mercury electrode

ping mercury electrode (Figure 4) and at a rotating tin microelectrode. In the prune juice, at least one and possibly as many as three cathodic depolarizers were observed, whereas none was detected in the grapefruit juice. The polarograms of the tomato juice could not be interpreted because of the large quantities of solids that could not be filtered out of solution.

As the electrochemical behavior of the juices at a mercury electrode is not necessarily the same as at a tin electrode, polarograms were also obtained at the latter. In this case, the current-voltage curves were considerably more complex, because of the anodic current from the oxidation of the tin and the cathodic current from the reduction of tin oxides. However, the data definitely showed that there was at least one substance present in prune juice that could oxidize tin, and that there did not appear to be any such substance present in grapefruit juice.

The presence of a depolarizer in prunes accounts for the fact that little or no hydrogen is evolved as the tin plate corrodes in this medium, and for the observed phenomenon that for all tin plate the rate of tin dissolution in prunes is a constant, if it is assumed that the reaction is a direct one between the tin and the depolarizer and that the steel base has no effect. In grapefruit and tomato juice, the situation is considerably more complicated and is still under study.

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