IMPACT OF ADDITIVES ON CORROSION RATE OF CANS FILLED WITH PIECES OF APRICOT

D.V. Tošković 1, M.B. Rajković 2 and D.D. Stanojević 1

Abstract: Polarization techniques are used for testing the impact of different compounds (additives) on tinplate corrosion, using pieces of apricot dipped in syrup with and without nitrate addition as electrolyte solution, at the same time using filled cans as electrolytic cell and operating electrode. This procedure determined the intensity of inhibiting tin dissolving with some of the used additives like sodium-benzoate, potassium-sorbate, sodium-lauril-sulphate and p-aminobenzoate acid. Adding these additives to canned pieces of apricot in syrup led to inhibiting of tin dissolving, which was experimentally proved.

Key words: tinplate, additives, sodium-benzoate, potassium-sorbate, sodium-lauril-sulphate, p-aminobenzoate acid.

Introduction

Tinplate is widely used in packing material production (Paine, 1996; Uhlig, 1958), especially for food packing (Crnčević, 1980). Food is made up of heterogeneous chemical content, often comprising or significant amount of water, organic acid, salt, nitrate, anthocyan, etc. is added. Some of these ingredients are a potential cause or accelerators of metal corrosion. In that case, metal ion concentration is increased, first of all tin and iron, which might affect the organoleptic quality of food as well as lead to can perforation.

One of the final operations in tinplate production is its chemical protection – chromatization (passivization). During this operation, a thin layer is formed on metal surface (passivization film) consisting of tin oxide, chrome oxide, and

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elementary chrome. It was proved that passivization film content on tinplate has a significant impact on metal corrosion process in contact with can content (Scherlock, 1976; Tošković and Rajković, 2000).

Determining corrosion rate, and corrosion characteristics of lacquered and not lacquered tinplate, is important from both theoretical and practical point of view. Corrosion measurement methods based on electrochemical methods (reciprocal relation electricity – potential) are applied in corrosion studies of these materials (Maercks et. al., 1969; Kleniewski, 1975; Scherlock et al., 1972; Alby-Yaron et al., 1977; Mansfeld et al., 1976; Oldhem and Mansfeld, 1971; Dražić i Vašić, 1985; Tsurumaru et al., 1980; Butler and Carter, 1963; Alby-Yaron et al., 1979; Catala and Cabanes, 1981; Gerischer und Tobias, 1978).

Although can corrosion problem cannot be completely eliminated, it can be reduced by introducing cans with lacquered inner surface, in which case the type of lacquer and its adhesion quality are very important. However, can lacquering cannot always prevent corrosion risk. On the other hand, some fruit and vegetables preserved in a completely lacquered can are exposed to changes in organoleptic quality, such as colour and aroma which are important for its commercial quality (Catala et al., 1977).

Different technical solutions have been suggested for reducing can corrosion problems to acceptable level, from both electrochemical and health aspect (Biston and Guerrier, 1973; Spruzen, 1976; Catala et al., 1979). Usage of non-lacquered tin is still recommended for some products, even in the case of tin contamination of can content.

A possible solution is adding substances in can content, which can significantly reduce aggressiveness of can content towards tinplate. This solution can be applied only if added substance is normal food component, or if it does not have negative effect on product quality or toxic effect on people.

Usage of corrosion inhibitors is a widely accepted technical solution used for metal protection and reducing tinplate corrosion. Many additives are suggested in patents as tinplate corrosion inhibitors: urea (Tanabe Seiyaki (patent), 1971), salicylamid, p-aminobenzoate acid, sodium-p-aminosalicylate and thryozin (Tanabe Seiyaki (patent), 1970), sodium-tiosulfate (Daiwa Seikan (patent), 1971), gelatin, ascorbic acid and sorbin acid (Levyanto and Putilova, 1972), L-lucile, L-arginine and their hydrochloride (Yamamoto and Morita, 1974) as well as L-asparagys acid, L-lizyl-asparagys acid, L-glutamic acid, L-lizyl-glutamic acid and its sodium chloride (Aizawa et al., 1975).

Mahadeviah (Mahadeviah et. al., 1976) adds karboksi-methanol-cellulose (0.5%) to mango juice, and Chang and Tsai (Chang and Tsai, 1978) add cistin 0.01-0.02% to canned asparagus juice to inhibit tin dissolving. Aforementioned patents relate to tinplate corrosion inhibiting without corrosion inhibitors. Nitrate ion presence in canned product causes faster tinplate corrosion, which can be seen through faster tin dissolving (Maršal et al., 1977).
Several authors pointed to the presence of substances inhibiting tin dissolving induced by nitrate ion presence in some products like cabbage, turnip and other from *Cruchipherea* family (Emilsen et al., 1974). Board and Holland (Board and Holland, 1969) attributed inhibition effect to modifying the quality of tinplate surface blocking nitrate ion reduction on the surface. The same authors also tested inhibiting effect of certain additives and established that carbon disulfide, trithioformaldehyde and diphenilthiourea, among others, almost certainly reduce tin dissolving induced by nitrate.

Using electrochemical techniques, Sherlock and Britton (Sherlock and Britton, 1973) gave a survey of numerous substances with potential inhibiting effect and established that sodium-lauril-sulphate and some naftil-sulfonat showed better efficiency. Albu-Yaron and Semal (Albu-Yaron and Semal, 1976) got positive results using sodium-benzoate, while Blundstone used allylthiourea (Blundstone, 1978). All authors did their research on model solutions as a test medium, except in several cases when usage on natural products was tested.

This paper shows the results of testing the usage of different additives for reducing corrosion of non-lacquered tinplate can filled with pieces of apricot dipped in syrup.

Using the cans lacquered inside prevents tin dissolving, however, pieces of apricot in lacquered cans get brown colour and lose in their quality during storage. Aforementioned changes have the effect on product quality after six months, which is the longest time limit recommended for packing this content in the inside-lacquered cans.

**Materials and Methods**

**Polarization tests**

Polarization tests (measurements) were carried out in the trielectrode system, using potentiostate/galvanostate (PAR model 173) and X – Y writer (HEWLETT PACKARD 7046A).

Cans made of non-lacquered tinplate were used in this study. Tin plate was 0.26 mm made in tinplate factory "Sartid 1913" A.D. "Beli limovi" in Šabac. Cans were made in «Limprodukt» factory from Novi Sad, filled in "Šapčanka", Šabac. The tested can (Ø 99 mm, T-3 with tin layer 11.2/5.6 g/m²) was working electrode and electrolytic cell at the same time. Can content (pieces of apricot in syrup) represented working electrolyte.

Electrolytic cell as working electrode was prepared by removing original metal cover from the can and then by putting a plastic cover with holes, where small tubes for nitrogen and electrodes were inserted: saturated calomel electrode was used as a reference electrode (*Saturated Calomel Electrode*, SCE), platinum
electrode (Pt) was supporting the electrode. Everything was well sealed with silicone, so that cell could not come in touch with oxygen from the air. In the middle of working electrode, at the level of Pt and SCE electrode, the contact of working electrode with potentiostat was welded, and then pure nitrogen release was adjusted, so that bubbling would not disturb the experiment.

All experiments were carried out in pure nitrogen stream prepared in a way so that extra pure nitrogen was passed through gas purifying solution, then through columns filled with P2O5 and through column with molecule size 3-10^{-10} m in size. Nitrogen purifying solution consisted of ammonium-metha-vanadate (NH₄VO₃), HCl, 3 times distilled water, with 25 g of amalgamized zinc (cleanlinesss 99.999) at the bottom of the rinser (Trassati, 1971).

Before measuring, can (electrolytic cell) content was deaired with pure nitrogen. Deairation started 12 hours before measuring and carried on during measuring.

Can content was prepared according to standard industrial practice and was stored with previous adding of potential corrosion inhibitor (additive).

Potentiodynamic anode polarization is a characteristic of each metal sample seen through its specific potential-current relation, with sample potential slowly moving towards positive values.

Polarization resistance is defined by using cathode potential of 10 mV for 8 minutes. Cathode polarization curve was achieved starting from 300 mV potential for 10 minutes, potential reduction of 25 mV/min. Anode potential is achieved from reaching the corrosion potential by polarization in anode direction.

Storing tests

Tinplate cans were filled with apricot pieces with added substances (additives) having the capacity of corrosion rate inhibition, warmed in sterilizator on 83°C for 11 minutes, and cooled to 40°C. One lot of cans was exposed to polarization tests immediately after stabilization.

Storing tests were carried out on several lots of canned products containing different concentration of tested additives (Table 1).

Cans were stored at room temperature (18°-22°C). During can storage, lasting 1 year, contents of tin, iron and lead in product (can content) were measured by the method of atomic absorption spectrophotometer using Perkin Elmer 5100 PC.

Results and Discussion

Electrochemical results

In previous papers (Tošković, Rajković i Lačnjevac, 1999a; Tošković, Rajković i Lačnjevac, 1999b; Tošković i Rajković, 2002; Tošković, Rajković and Ćirić, 2002; Тошкович et al., 2002) the authors
presented the technique of getting polarization curves in food cans, using filled can as working electrode and electrolytic cell at the same time, and its content as working electrolyte, where SCE was used as a reference electrode, while platinum wire was used as a supporting electrode.

This technique can be used to determine natural products relation to tinplate, and their relative aggressiveness.

Measurings were done after the filled can was deaired for 12 hours.

Polarization curves for samples stored for 1 year, with different additives, without nitrate, were achieved in the same way.

Polarization curves for tinplate cans were achieved in electrolyte made of syrup with pieces of apricot. Substances were added in electrolyte where the efficiency of corrosion inhibition was the subject of testing. Alternatively, 50 ppm of nitrate was added in electrolyte in order to test the possibility of faster detinning inhibition caused by nitrate ions.

Based on these measurements, Tafel line was constructed and necessary electrochemical parameters were calculated: $E_{\text{corr}}$ (corrosion potential), $i_{\text{corr}}$ (corrosion current), $\beta_c$ and $\beta_a$ (incline of Tafel lines).

Polarization curves for apricot pieces in syrup with alternative and combined adding of potassium-sorbate and nitrate-ion are shown in Fig. 1., while the results obtained in the experiments by using four additives are shown in Table 2.

![Fig. 1. - Polarization curves of tinplate can filled with apricot pieces dipped in syrup, with following signs: 
----- no additives; ◀ - 0.1% potassium-sorbate; ● - 50 ppm NO$_3^-$; 
♦ - 50 ppm NO$_3^-$ and 0.1% potassium-sorbate](image-url)
Selection of additives for testing was done according to the study of a wide range of substances, using 0.1 mol/dm³ citrate solution of buffer pH = 3.50 as electrolyte (Modić, 2001).

<table>
<thead>
<tr>
<th>Additive sign</th>
<th>International (E/INS)</th>
<th>Official additive name</th>
<th>Group (CA)</th>
<th>Additive origin</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.21</td>
<td>E202</td>
<td>potassium sorbate</td>
<td>A(1)</td>
<td>P,S</td>
<td>Ko</td>
</tr>
<tr>
<td>2.3</td>
<td>E211</td>
<td>sodium benzoate</td>
<td>A(1)</td>
<td>P,S</td>
<td>Ko</td>
</tr>
<tr>
<td>13d.3</td>
<td>487 *</td>
<td>sodium-lauril-sulfate</td>
<td>B</td>
<td>–</td>
<td>PoS</td>
</tr>
<tr>
<td>2.1</td>
<td>E210</td>
<td>benzoic acid</td>
<td>A(1)</td>
<td>P,S</td>
<td>Ko</td>
</tr>
</tbody>
</table>

NOTE: Additives are shown according to group Codex Alimentarius (CA), group A(1), A(2), B, and their origin: P – natural, Pi – identical to natural, S – synthetic: Ko – preserve, PoS – supporting means in production process. Sign * means this additive is not on E list.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration (in mas.%)</th>
<th>$E_{corr}$ (mV)</th>
<th>$R_p$ (kΩcm$^2$)</th>
<th>$\beta_c$ (mV/logi)</th>
<th>$\beta_a$ (mV/logi)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>Protection effects (in %)</th>
<th>Protection effects (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-630</td>
<td>34.5</td>
<td>160.5</td>
<td>52.8</td>
<td>0.658</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-amino-benzoate acid</td>
<td>0.05</td>
<td>-639</td>
<td>60.1</td>
<td>174.0</td>
<td>41.1</td>
<td>0.431</td>
<td>34.5</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>-639</td>
<td>52.6</td>
<td>163.7</td>
<td>43.4</td>
<td>0.455</td>
<td>31.0</td>
<td>34.6</td>
</tr>
<tr>
<td>sodium-lauril-sulfate</td>
<td>0.01</td>
<td>-643</td>
<td>58.0</td>
<td>174.0</td>
<td>55.6</td>
<td>0.310</td>
<td>52.9</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>-636</td>
<td>35.0</td>
<td>168.3</td>
<td>45.9</td>
<td>0.477</td>
<td>27.4</td>
<td>-0.5</td>
</tr>
<tr>
<td>sodium benzoate</td>
<td>0.3</td>
<td>-662</td>
<td>66.3</td>
<td>154.4</td>
<td>46.2</td>
<td>0.367</td>
<td>44.1</td>
<td>48.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-649</td>
<td>59.9</td>
<td>146.8</td>
<td>56.8</td>
<td>0.420</td>
<td>26.0</td>
<td>43.6</td>
</tr>
<tr>
<td>calcium sorbat</td>
<td>0.3</td>
<td>-660</td>
<td>93.5</td>
<td>145.4</td>
<td>44.1</td>
<td>0.220</td>
<td>67.0</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-641</td>
<td>93.5</td>
<td>161.2</td>
<td>48.4</td>
<td>0.360</td>
<td>45.1</td>
<td>63.0</td>
</tr>
</tbody>
</table>

Quantitative results of inhibition effect for four selected additives are given in Table 2, as well as protection efficiency (in wt.%). These results show that all tested additives show inhibition effect on tinplate corrosion in apricot pieces in syrup with acceptable protection efficiency. Especially, adding 0.3 wt.% of potassium-sorbate leads to reducing the corrosion rate by 67%.
Results show that, regardless the fact that nitrate ions are added or not, adding the potassium-sorbate increases negative corrosion potential of the system, and decreases the bend of cathode polarization curve.

When nitrate ions are present in measuring concentrations, owing to their reductible character, the polarization curve is liable to sensitive bending with lower current density, and it is not following Tafel behaviour. In this case, the corrosion rate estimate cannot be done through crossing of Tafel lines. An alternative method is linear polarization technique. Using graphic method of linear polarization, corrosion current and corrosion potential are obtained in the crossing of Tafel lines (E = f (log i)). As it is shown in papers (Tošković, Rajković i Lačnjevac, 1999a; Tošković, Rajković i Lačnjevac, 1999b; Tošković i Rajković, 2002), corrosion current (icorr) calculated by this procedure is a good parameter for estimating real tin dissolving rate, and it can be used for evaluating inhibition effects of substances added in solution relating to original solution without additives.

Numerical processing of data obtained by polarization measuring means computer processing of experimental results (Ivaniš, 1989). As a result of polarization measuring comes the group of n-pairs of data ei and ii, where the current i = E (l, ..., n). Each data resulted from experiment contains a certain measuring error, thus creating a difference from linear logarithm dependence. In order to avoid wrong conclusion, which could be reached by determining mutual position of neighbouring points, it is necessary to determine measuring results approximation before determining function bending. Approximation resulted from the smallest square method.

Comparative method for corrosion current determining is the polarization resistance method (Metikoš-Huković, 1986; Stern and Geart, 1955; Mansfeld, 1973). Polarization resistance, Rp is polarization curve bend on corrosion potential, $\frac{\Delta E}{\Delta I}$.

Polarization resistance measuring (Rp) of complex material, like tinplate, according to natural products, like vegetables (or fruit), represents a practical problem. While these processes have small (low) corrosion rate, polarization resistance changing with time is high. System stabilization requires a long period of time (over 100 hours) (Massini, 1976).

Effective value of polarization resistance (Rp) resulted from applying 10 mV during 8 minutes is a good evaluation of the system corrosion intensity. Additionally, the value of icorr calculated from Rp, $\beta$c and $\beta$a, using Stern and Garry equation, is of the same system of values as the one resulted from polarization lines crossing. Low reproduction of Rp measuring is the result of unreproductivity of tinplate surface, as well as oxygen traces in solution even if it is nitrogen atmosphere.
Small variations in solution, with substances affecting tinplate corrosion rate, can lead to measurable change of $R_p$ value, giving the possibility of quantification and comparison of such effects. Polarization resistance can be used as a parameter for direct evaluation of system corrosion rate. $R_p$ value is also used for protection efficiency estimate of tested substances, which is shown in Table 2. Inverse $R_p$ value is used in practice leading to easier interpretation of results and comparison of corrosion effects.

It can be seen that the value of protection efficiency calculated from $R_p$ is of the same system of value as the one resulted from $i_{corr}$ value. One anomaly is seen for sodium-lauril-sulfate with concentration of 0.005 wt.% with great difference between protection efficiency percentage resulting from $i_{corr} = 27.4$ wt.% and the one resulting from $R_p = -0.5\%$.

The same parameter $R_p$ was used for testing the protection effect of test substances while adding 50 ppm of nitrate-ion into product, with the results shown in Table 3.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration (in %)</th>
<th>Corrosion potential $E_{corr}$ (mV)</th>
<th>Polarization resistance $R_p$ (kΩ/cm²)</th>
<th>Protection efficiency (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without additives</td>
<td>–</td>
<td>- 620</td>
<td>9.8</td>
<td>–</td>
</tr>
<tr>
<td>p-aminobenzoate acid</td>
<td>0.05</td>
<td>- 627</td>
<td>14.5</td>
<td>32.7</td>
</tr>
<tr>
<td>sodium-lauril-sulfate</td>
<td>0.01</td>
<td>- 624</td>
<td>9.2</td>
<td>- (6.5)</td>
</tr>
<tr>
<td>sodium-benzoate</td>
<td>0.3</td>
<td>- 649</td>
<td>17.8</td>
<td>45.1</td>
</tr>
<tr>
<td>potassium-sorbate</td>
<td>0.3</td>
<td>- 663</td>
<td>24.9</td>
<td>60.7</td>
</tr>
</tbody>
</table>

Measuring results, shown in Table 3, show that 3 of 4 additives act like nitrate induced corrosion inhibitors, while sodium-lauril-sulfate shows accelerator effect (protection efficiency –6.5). Percentage of protection efficiency is the same in all the cases as the one established without nitrate ion presence.

Based on the shape of anode and cathode polarization curves for all tested additives, it can be concluded that unlacquered tinplate corrosion is caused by additives affecting cathode corrosion semi-reaction. Anion additive character points to possible forming of adsorption film in the border of phases (metal surface/tinplate-electrolite), thus causing cathode reaction to develop slowly.

**Actual inhibiting effect in canned product**

Potential inhibiting effect on tin dissolving derived from polarization study of tested additives is to be confirmed by determination of practical effects in tinplate cans which were stored.

That is the reason why unlacquered tinplate cans were produced in usual industrial conditions, filled with apricot pieces in syrup, with certain additives
added. Metal (Sn, Fe, Pb) dissolving control and tinplate corrosion rate were done periodically during one-year storage period at room temperature.

Tin content in the product at the end of storage period, determined on the whole product (hard plus liquid in the ratio of 2:1), as well as appropriate values of protection efficiency are shown in Figures 2 and 3.

Fig. 2. - Protection efficiency of certain additives in canned pieces of apricot in syrup, where □ is dissolved tin; ■ protection layer efficiency

Fig. 3. - Protection efficiency of certain additives in canned pieces of apricot in syrup with addition of 50 ppm NO₃⁻, where □ is dissolved tin; ■ protection layer efficiency
Three of tested additives showed the inhibiting effect in relation to present nitrate ions (Figure 3). Sodium-lauril-sulfate caused corrosion acceleration with both applied concentrations. Best results came from sodium-benzoate in concentration of 0.3 wt.% with efficiency protection of 27%.

There is a difference between protection efficiency values obtained from polarization measurements (Table 2) and actual values obtained from storage tests (Figure 2). Although there is a correlation between these values, actual results are lower, which is explained by the fact that inhibiting efficiency declines in time.

Aforementioned difference can be explained by taking into consideration the fact that parameters obtained from polarization measurements are only the estimate of initial corrosion rate. In real corrosion process corrosion rate decreases in time. Actual corrosion intensity, calculated from tin dissolving data, is more than 100 times lower than initial value; corrosion rate is influenced by numerous factors in connection with canned product and tinplate quality (Catala and Duran, 1976).

Presence of 50 ppm of nitrate ions caused high corrosion rate, tin content in canned product was four times higher after the storage period of one year. All four tested additives had the effect on corrosion reduction caused by nitrate ion presence. The best results were shown by p-aminobenzoate acid presence, with protection efficiency of 32%, added in 0.05 wt.% concentration.

The unexpected result is low inhibiting power of sodium-lauril-sulfate in relation to nitrate corrosion, since it was reported that this substance shows extremely high inhibiting efficiency (higher than 90%) when tested in model solutions (Sherlock and Britton, 1973; Catala and Cabanes, 1980). Such behaviour can be the consequence of lauril-sulfate interaction with certain food components.

It is necessary to mention that both in the presence and absence of nitrate ion, tin dissolving inhibiting did not affect iron and lead dissolving in canned product, the content of these metals being similar in all samples: 1-3 ppm for Fe and 0.3-0.5 ppm for Pb.

**Conclusion**

Although inhibiting efficiency of tested additives was not very high, it is reliable enough to be applied in practice. Other substances, mentioned in literature, can produce better results, but they cannot be used as additives in food, which was not the case with additives used in this study.

On the other hand, negative effect on organoleptic qualities of can content was not registered with used concentrations, therefore they can be used in food products.
REFERENCES

Impact of additives on cans corrosion


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UTICAJ ADITIVA NA BRZINU KOROZIJE LIMENKE NAPUNJENE KOMADIMA KAJSIJE

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Rezime

Primenom polarizacionih tehnika ispitivan je uticaj različitih supstanci (aditiva) na koroziju belog lima od kojeg su napravljene limenke, primenjujući kao rastvor elektrolita komade kajsije u sirupu sa i bez dodatka nitrata, uz istovremeno korišćenje napunjene konzerve kao elektrolitičke čelije i kao radne elektrode.

Ovim postupkom je određena jačina inhibiranja rastvaranja kalaja nekim od primenjenih aditiva, kao što su: natrijum-benzoat, kalijum-sorbat, natrijum-lauril-sulfat i p-amino-benzoeva kiselina. Dodatkom ovih aditiva u konzervisane komade kajsije u sirupu došlo je do inhibiranja rastvaranja kalaja što je eksperimentalnim putem i dokazano.


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