

Corrosion of Foodstuffs Cans in Saline Solutions Containing Preservative Material

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ABSTRACT—This work involves try to study the corrosion behavior of food can in 200 ppm sodium benzoate which use as preservative material in the absence and presence of three concentrations of sodium chloride (0.001, 0.01, and 0.1 M) to study corrosion resistance of can to pitting due to penetrate chloride ions the passivity layer. This study was performed using potentiostat at scan rate 3 mV.sec⁻¹. Corrosion parameters were measured using Tafel extrapolation method, in addition to calculate corrosion resistance and corrosion rate. The data of corrosion indicate that using sodium benzoate as preservative material give acceptable corrosion resistance of foodstuffs can. The presence of 0.001 and 0.01M NaCl don't affect on the corrosion behavior of cans, while 0.1M of NaCl in 200 ppm sodium benzoate solution lead to increases of corrosion current density. The increases in corrosion current density may be due to penetrate chloride ions the protective film and the competitive role for chloride and benzoate ions to bonding with metal surface. Also the results of polarization resistance indicate that the resistance decreases only in the presence of 0.1M saline solution with 200 ppm sodium benzoate. Therefore, must avoid the high salinity in the food cans to avoid corrosion of cans and release the toxic metallic ions the foods and drinks.

Keyword—Food cans; corrosion of cans; sodium benzoate.

1. INTRODUCTION

Preservatives are meant to prevent spoilage caused by microbial growth. The most common preservative is sodium benzoate, which is tasteless and odorless at the appropriate concentrations and effective against the growth of mold, fungus, and bacteria. The recommended concentration is 150–200 ppm. It is effective in sour products (the non-ionized form is the active form). Preservatives should not be added to products, like cider and beer, which are pasteurized to kill bacteria [1].

Sodium benzoate has the chemical formula NaC₆H₅CO₂. It is the sodium salt of benzoic acid and exists in this form when dissolved in water. It can be produced by reacting sodium hydroxide with benzoic acid. Sodi. It is bacteriostatic and fungistatic under acidic conditions. It is most widely used in acidic foods such as salad dressings (vinegar), carbonated drinks (carbonic acid), jams and fruit juices (citric acid), pickles (vinegar), and condiments. It is also used as a preservative in medicines and cosmetics. As a food additive, sodium benzoate has the E number E211 [2].

This research investigates effect of sodium benzoate in saline solutions on corrosion behavior of food cans. Gryscavage et al. indicated that using a combination of phosphates, nitrite, silica, amine, and patented polymer technology — resulted in excellent corrosion protection of the cooker chain and associated equipment. The new monitoring techniques employed have allowed for better monitoring of the conditions within all stages of the cooker. Corrosion rates have remained very low with an average rate of 1.6 mils (0.04 mm) per year. Reducing the initial corrosion rates from as high as 54 mils (1.37 mm) per year has resulted in dramatic improvement in system operation. It is expected that by maintaining the existing chemical treatment program, replacement of the chains in the cooker will not be required for many years [3].

Certain patent shows that corrosion of galvanized steel in the presence of water and oxygen is known to occur in galvanized steel cans containing aqueous products. A problem with galvanized steel aerosol cans is that they fail to

operate after the corrosion sets in. In extreme cases, corrosion can result in perforation of the aerosol containers with loss of product. Commercially available corrosion inhibitors provide corrosion resistance for short periods of time but are generally not as effective for longer duration [4].

Antonela et al. studied corrosion inhibition with different protective layers in tinplate cans for food preservation, they show that when essential onion oil EOO as the protective layer instead of dioctyl sebacate oil DOS oil was used, tinplate porosity, measured electrochemically ($7.58 \pm 1.97 \mu\text{A cm}^{-2}$ and $23.0 \pm 1.3 \mu\text{A cm}^{-2}$, respectively), and iron coating mass, calculated from atomic absorption spectroscopy AAS data ($1.52 \pm 0.15 \text{ mg m}^{-2}$ and 3.14 ± 0.42 , respectively), was much lower indicating better corrosion protection. At higher storing temperature (36°C) the addition of EOO to canned tomato purée enhanced the formation of hydrogen with time. The increasing volume fraction of H_2 (from 34.0 to 90.9% for cans without nitrates, and from 33.8 to 89.2% for cans with nitrates) is an indicator that corrosion takes place [5].

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Chemicals

Samples of foodstuffs can were cut to sheet with surface area of 4cm^2 to electrochemical test. Chemical composition of can was investigated using spectromax as shown in table (1). Basic electrolytes were saline solutions prepared by dissolved sodium chloride in distilled water with three concentrations (0.001, 0.01, and 0.1 M) containing 200 ppm of sodium benzoate.

2.2 Electrochemical Test

The electrochemical standard cell used in this work was locally fabricated according to the ASTM standard G5-94 with provision for working electrode (foodstuffs can), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an saturated calomel electrode SCE reference electrode.

Potentiodynamic and cyclic polarization measurements were carried out with WINKING MLab 200 Potentiostat from Bank-Elektronik. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate $3 \text{ mV}\cdot\text{sec}^{-1}$. Polarization experiments were started when the rate at which open circuit potential (E_{ocp}) changed was less and more 200mV. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slopes by Tafel extrapolation method. From the values of Tafel slopes and corrosion current density, the polarization resistances values can be calculate according to Stern-Geary equation. While experimental parameters for cyclic polarizations were obtained directly from SCI electrochemical software of potentiostat.

3. RESULTS AND DISCUSSION

Fig. (1) shows the variation of open circuit potential with time for foodstuffs can in 200 ppm sodium benzoate in the absence and presence of sodium chloride with three concentrations (0.001, 0.01, and 0.1M), this figure indicates that the presence of sodium chloride shift E_{oc} to noble direction which may due to produce certain stable complex between benzoate and chloride with metal of can in addition to behave the benzoate ions as barrier between material and environment. Fig. (2) shows the polarization curves for can in 200 ppm sodium benzoate in the absence and presence of sodium chloride with three concentrations, these curves show the cathodic and anodic regions. At cathodic sites, reduction of oxygen to produce hydroxide ions can occur. While at anodic sites dissolution of metals can occur after destroy the coating layer.

Corrosion parameters were measured using Tafel extrapolation method and the data are listed in table (2), these data indicate that using sodium benzoate as preservative material give acceptable corrosion resistance of foodstuffs can. Generally in benzoate solutions, more than one pit was initiated and the overlapping of the transient behavior for each pit masked the kinetics of each individual pit [6]. Also benzoate ($\text{C}_6\text{H}_5\text{COO}^-$) ions act as blocking inhibitors by forming insoluble precipitates. It was noticeable that such deposited formed at a slight distance from pits after initiation. This inhibitor arrested pit propagation at an early stage rather than prevented pit initiation [7]. The bulky molecules limit the diffusion of oxygen to the surface or they trap the metal ions on the surface, reducing the rate of dissolution, while inorganic oxidizing substance that promote the passivity on the surface by shifting the corrosion potential in the noble direction.

The mechanism of inhibition starts with the absorption of benzoic acid into the cell. If the intracellular pH changes to 5 or lower, the anaerobic fermentation of glucose through phosphofructokinase is decreased by 95%, [8] thereby inhibiting the growth and survival of micro-organisms that cause food spoilage.

The presence of 0.001 and 0.01M NaCl don't affect on the corrosion behavior of cans, while 0.1M of NaCl in 200 ppm sodium benzoate solution lead to increases of corrosion current density. The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the value of (i_{corr}) results in an enhanced value of the corrosion rate on pure kinetic ground.

The increases in corrosion current density may be due to penetrate chloride ions the protective film and the competitive role for chloride and benzoate ions to bonding with metal surface. Three main reasons for the specific effect of chloride ion appear to be, (a) Its ability to increase the activity of hydrogen ion in the pit electrolyte, (b) Its ability to form salt layer at low pH at the bottom of the pit, and (c) Ability to form complexes with cations and hydroxides [9].

The ratio (E_{corr}/i_{corr}) thus corresponds to the resistance of the metal/solution interface to charge-transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed. The polarization resistance (R_p) may be defined as [10]:

$$R_p = \frac{d\eta}{di} = \frac{d(E-E_{corr})}{di} = \frac{E_{corr}}{i_{corr}} = \frac{RT}{Fi_0} \dots\dots(1)$$

Where E and E_{corr} are the applied and corrosion potential (Volt) respectively, i is the current density ($A.cm^{-2}$). i_0 is the equilibrium exchange current density ($A.cm^{-2}$). The reaction resistance (R_p), which mainly depends upon the equilibrium exchange current density (i_0) determines what may be termed the polarizability, i.e., what overpotential ($\eta=E-E_{corr}$) a particular current density needs or produces[11, 12].

The polarization resistance (R_p) was also determined in another way from Stern- Geary equation, where [13, 14]:

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a \cdot b_c}{2.303 \cdot i_{corr} \cdot (b_a + b_c)} \dots\dots(2)$$

where b_c and b_a are cathodic and anodic Tafel slop respectively. The values of R_p have been calculated from eq.(2), which are presented in table (2). The results of polarization resistance indicate that the resistance decreases only in the presence of 0.1M saline solution with 200 ppm sodium benzoate. Therefore, must avoid the high salinity in the food cans to avoid corrosion of cans and release the toxic metallic ions the foods and drinks.

Corrosion rate values can be calculate from the following formula [15] using corrosion current density (i_{corr}), equivalent weight of corroded alloy (56 gm) and density of alloy (7.8 gm/cm^3).

$$C_R(mm/y) = 3.27 \frac{e}{\rho} i_{corr} \dots\dots(3)$$

The results of corrosion rate agreement with the results of corrosion resistance and can be seen that 0.1M of sodium chloride with 200 ppm sodium benzoate increases the rate of corrosion as shown in figure (4) due to destroy the protective layer which formed by benzoate ions and penetrate the chloride ions this layer.

4. REFERENCES

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Table 1: Chemical composition of used can in this work.

<i>Metals</i>	V	Mn	Sn	Fe
<i>Wt%</i>	0.19	0.47	0.61	97.25

Table 2: Corrosion parameters of food can in 200 ppm sodium benzoate containing three concentrations of sodium chloride at room temperature.

<i>Environment</i>	<i>Open circuit potential (E_{oc}/mV)</i>	<i>Corrosion potential (E_{corr}/mV)</i>	<i>Corrosion current density (i_{corr}/μA.cm⁻²)</i>	<i>Tafel slope (mV.dec⁻¹)</i>		<i>Corrosion resistance x10³ (R_p/Ω.cm²)</i>	<i>Corrosion Rate mpy</i>
				<i>-b_c</i>	<i>+b_a</i>		
Sodium benzoate	-88	-88.1	6.68	141.8	132.3	4.455	3.119
Sodium benzoate + 0.001N NaCl	+10	+10.9	0.958	74.2	74.9	16.917	0.642
Sodium benzoate + 0.01N NaCl	+133	+110.6	2.48	118.7	120.9	10.501	1.158
Sodium benzoate + 0.1N NaCl	-82	-90.5	10.35	115.5	111.4	2.382	4.833

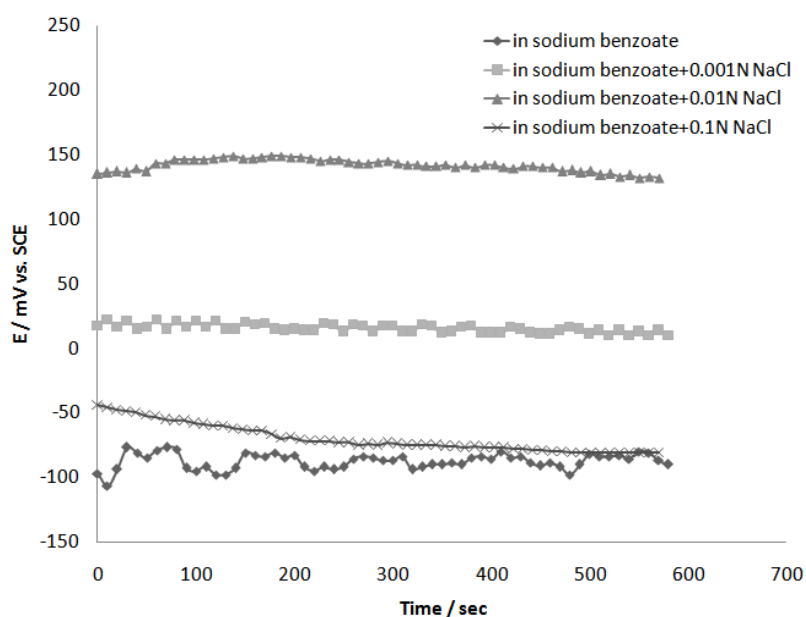


Figure 1: The variation of open circuit potential – time for food cans in saline solutions containing 200 ppm sodium benzoate.

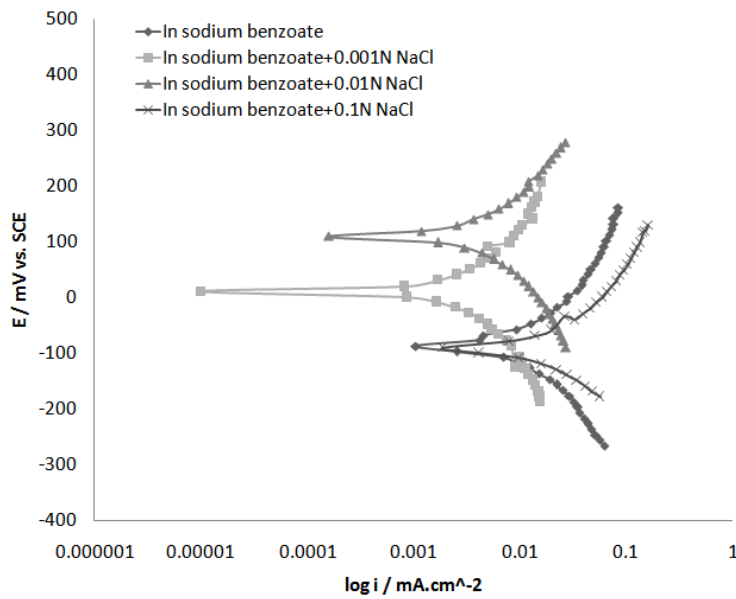


Figure 2: Potentiodynamic curves for food cans in saline solutions containing 200 ppm sodium benzoate.

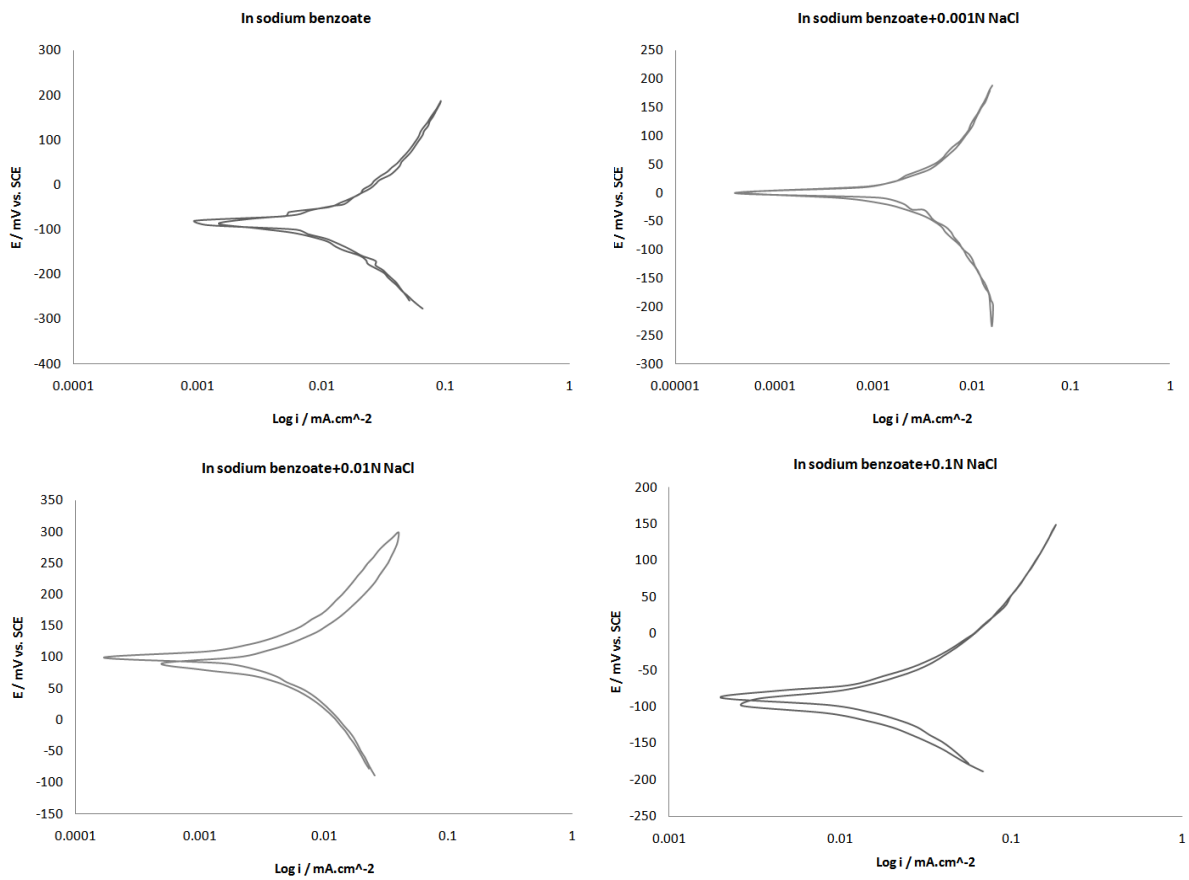


Figure 3: Cyclic polarization curves for food cans in saline solutions containing 200 ppm sodium benzoate.

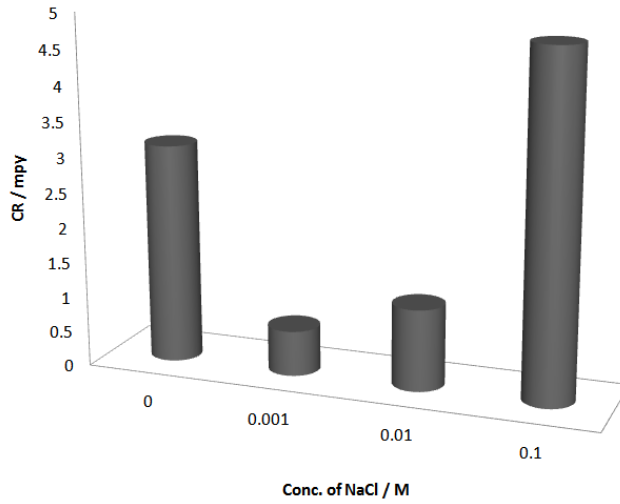


Fig. 4: Relationship between corrosion rate and concentration of saline solution in presence of 200 ppm sodium benzoate.