

DETERMINATION OF THE CORROSION RATE IN TINS FILLED WITH PEAS AND STRING BEANS DURING STORAGE

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Abstract: This paper presents the results of examination of the corrosion behaviour of electrolytic tinplate in model solutions of salts in liquid contents (fills) of peas and string beans tins. The tins have been stored at the temperature of 25 °C during the period of 18 months. The obtained results show that the corrosion currents and consequently corrosion rates, too, have higher values in the liquid contents (fills) of the tins than in the pure model solutions. Corrosion currents decrease noticeably in nitrogen atmosphere which speaks in favour of packaging of foodstuff in inert atmosphere.

Key words: string beans, peas, tinplate, corrosion currents, corrosion rates, inert atmosphere.

Introduction

Foods, which are kept in the tinplate packing, can be low-alkaline, such as certain kinds of boiled vegetables and meat, or sour, such as products of a large number of tinned fruit, yogurt and many others. Almost all kinds of fruit and also some other sorts of food contain a sufficient amount of acids which react with the metal material of a tin. These acids are quite corrosive regarding the small amount of the present H⁺ ions. Although their corrodibility is lower than that of inorganic acids, the concentration of H⁺ ions being sufficient for a fast attack on the packaging material, especially in the presence of oxidizing sub-

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stances in the liquid content (of tins) or in the presence of the remaining oxygen from air, upon closure of a tin.

Neutral salts, such as NaCl, are usually less aggressive compared with neutrally oxidizing salts (NaNO_2 and NaNO_3) as well as with acid and alkali salts (Gerischer and Tobias, 1978). Small concentrations of nitrites, already from 0.01 mg, lead to fast detinning inside tins filled with sour contents. These corrosion processes develop with the relatively slow reduction of nitrites and the fast formation of NH_4^+ ions.

The factors which affect and contribute to the corrodibility of liquid contents (fills) in tins filled with peas and string beans are: concentration of NaCl, presence of oxidizing substances, temperature during the process of sterilization and pasteurization, addition of different salts into the solution to preserve the smoothness of grains (peas) and to prevent the wrinkleness of grains, and to maintain the green colour of chlorophyll of string beans, or at least to preserve, to some extent, the shade of the green coloured product acceptable for a manufacturer. All the factors together characterize the fill in which vegetables are kept during storage and which produce a corrosive effect on the material the tin is filled with.

During this research the corrosion behaviour of electrolytic tinfoil in the model solution of salts and in liquid contents (fills) of peas and string beans tins have been examined and the corrosion rates during the storage have been determined and calculated. The methods of corrosion examinations based on the electrochemical methods (the current potential relation) usually used in the study of corrosion of the tinfoil (Alby-Yaron et al., 1979; Butler and Carter, 1963; Catala and Cabanes, 1981; Dražić i Vaščić, 1985; Kamm and Willey, 1961; Mansfeld et al., 1986; Nagy et al., 1980; Niketić-Aleksić, 1994; Oldhem and Mansfeld, 1971; Priručník, 1970; Tošković, Rajković i Lačnjevac, 1999a, 1999b).

Material and Methods

Experimental tests were carried out on the samples of electrolytic tinfoil ($2.8/2.8 \text{ g/cm}^2$ of tin on both sides) manufactured in the factory for tinfoil production "Sartid 1913" d.d. at Šabac. The tins of commercial production were made of tinfoil ("Limprodukt", Novi Sad) and filled with peas and string beans (DP "Šapčanka", Šabac). The tins were stored at the temperature of $25 \text{ }^\circ\text{C}$ during the period of 18 months. After the time of 1, 6, 12 and 18 months, the samples were cut out of the material of the tins and used for making electrodes of the surface of 1 cm^2 . Nonlacquered tins were tested, while the edges and the backs of those electrodes were protected by epoxy resin.

Model solutions of salts were made of substances of p.a. purity (d.d. "Zorka-Farmacija", Šabac) in the concentration at which they were usually found in tins of peas and string beans, i.e. 2.5 wt. % NaCl with the addition of 0.015 wt. % NaNO_3 . Liquid contents (fills) were taken from the already stored tins of peas and string beans.

The determination of the corrosion current and potential was carried out by the galvanostatic polarization procedure applying the Evans and Hoar method (Kamm and Willey, 1961) in the electrolytic cell with three electrodes and with tinplate working electrode, of the aforementioned quality and make, with the contraelectrode made of REMCO iron and saturated calomel electrode (SCE) as a referent electrode.

The measurements were carried out in air and in the atmosphere of nitrogen which had streamed through the solution for 30 minutes before the measurements began. Extra pure nitrogen (99.999 vol. %) was passed through the gas purification solution, then through columns filled with P_2O_5 and finally through the column with molecule sieves sized $3 \cdot 10^{-10}$ m. The solution for nitrogen purification consisted of ammonium meta vanadates (NH_4VO_3), HCl, tridistillation water ($3 \times D_{vod}$) while 25 g of amalgamated zinc, of the purity 99.999 wt. % was at the bottom of the rinsing apparatus (Trassati, 1971).

Corrosion currents and potentials were defined from the cross section of the polarization curves. The potentials were calculated by the equation (1):

$$\frac{m}{\rho \cdot S \cdot \tau} = \frac{M}{\rho \cdot n \cdot F} \cdot i_{corr} \quad [m/\text{hour}] \rightarrow [mm/\text{year}] \quad (1)$$

where: m - mass (in g); ρ - specific density of tinplate which is corrosive (the value for tin is 7.285 g/cm^3 , whereas the value of 7.855 g/cm^3 is taken for tinplate); i_{corr} - corrosion current (A/cm^2), M - molal mass of tin (118.7 g/mol); F - Faraday constant, 96487 (C/mol) ; S - surface (in m^2); τ - time (in h); n - number of electrons.

Results and Discussion

Table 1 presents the chemical composition of string beans and peas (in wt. %) (Nagy et. al., 1980).

Tab. 1. - Chemical composition of string beans and peas (in wt. %)

| Product | Carbohydrates | Proteins | Fats | Ash | Water |
|--------------|---------------|----------|------|-----|-------|
| string beans | 7.6 | 2.4 | 0.2 | 0.7 | 89.1 |
| peas | 17.0 | 6.7 | 0.4 | 0.9 | 75.0 |

Table 2 shows the results of pH value change during storage in both kinds of tins and pH values of model solutions of salts.

Tab. 2. - The pH values of the analysed solutions

| Solution | 1 day | 2 months | 7 months | 12 months | 18 months |
|---------------------------------------|-------|----------|----------|-----------|-----------|
| 2.5 wt. % NaCl | 5.92 | - | - | - | - |
| 2.5 wt. % NaCl + 0.015 wt. % $NaNO_3$ | 5.88 | - | - | - | - |
| fill of peas | 6.24 | 6.23 | 6.22 | 6.21 | 6.22 |
| fill of string beans | 5.45 | 5.29 | 5.14 | 5.10 | 5.06 |

The change of pH value in the liquid contents of the tins during storage is not significant. The higher pH value of the liquid contents (fills) of peas can be attributed to the increased content of alkali salts added to peas during short boiling, in order to preserve the green colour of peas. The stability of pH value of the fills of peas is probably caused by a higher content of carbohydrates and proteins.

The increased acidity of the fills of string beans by the whole unit of pH value and its increase during storage can be explained by enzymatic activity of *methylesterase*, whose effect produces deesterification of carboxylic groups, so that their dissociation occurs and thereby pH value decrease by 0.4 of the unit during 18 months' storage (Van Vliet and Wolstra, 1980).

Figure 1 shows the diagrams of tinplate and iron polarization in model solutions of NaCl and NaCl with the addition of NaNO₃, and in the liquid contents (fills) of the tins filled with peas and string beans, determined on the first day of the storage, in the presence of air.

The highest values of corrosion currents of tinplate were obtained in the fill of string beans, whereas the lowest ones in the model solution of the mixture of salts. The corrosion process was under control in all the tested solutions, except in the model solution composed of NaCl and NaNO₃, where the corrosion process was under the mixed anodic and cathodic control in the corrosion couple - cell.

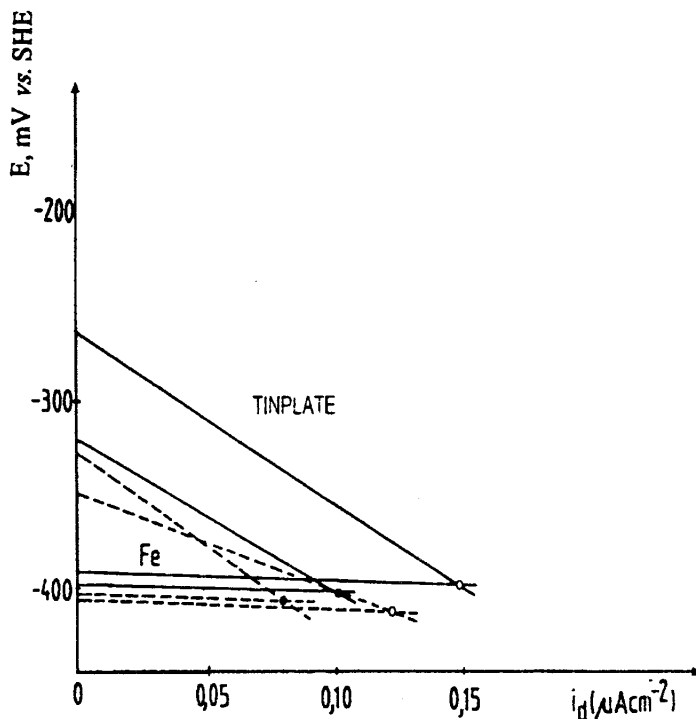


Fig. 1. - Relation of current and potential at tinplate polarization, in the fill of peas (•) and string beans (○) in air (-) and in nitrogen stream (- -) on the first day of storage

The diagrams of current and potential in both air and nitrogen atmosphere are displayed in Figure 2, where it can be seen that the corrosion rates are higher in the fills of tins of string beans in both analysed atmospheres than the corrosion rates determined in the fills of tins filled with peas.

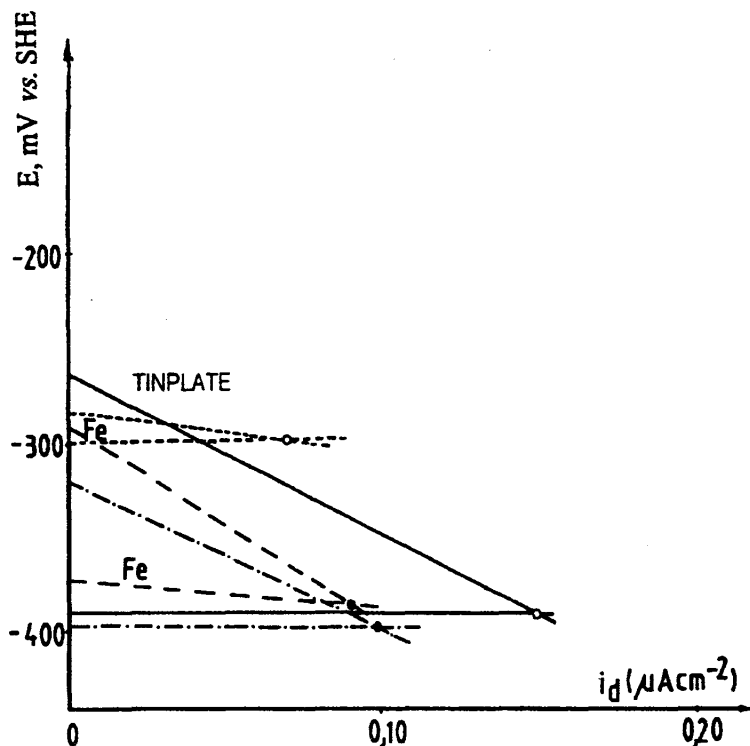


Fig. 2.- Relation of current and potential at tinplate polarization in air on the first day of the storage: fill of peas (---), fill of string beans (-), 2.5 wt. % NaCl (- - -), 2.5 wt. % NaCl + 0.015 wt. % NaNO₃ (- - - -).

The corrosion currents were lower in the solutions through which nitrogen was passed prior to each determination, whereby the effect of dissolved molecular oxygen on the corrosion process was removed.

Figures 3 and 4 show that the increase of corrosion currents in all the analysed media (solutions and fills) and in both kinds of gas atmosphere is the greatest during the first month of storage and after that the increase is, as a rule, almost linear, depending on the duration of storage. The highest corrosion currents are in the solution NaCl, and the lowest in the mixtures of NaCl and NaNO₃. The corrosion currents are noticeably higher in air than in nitrogen stream.

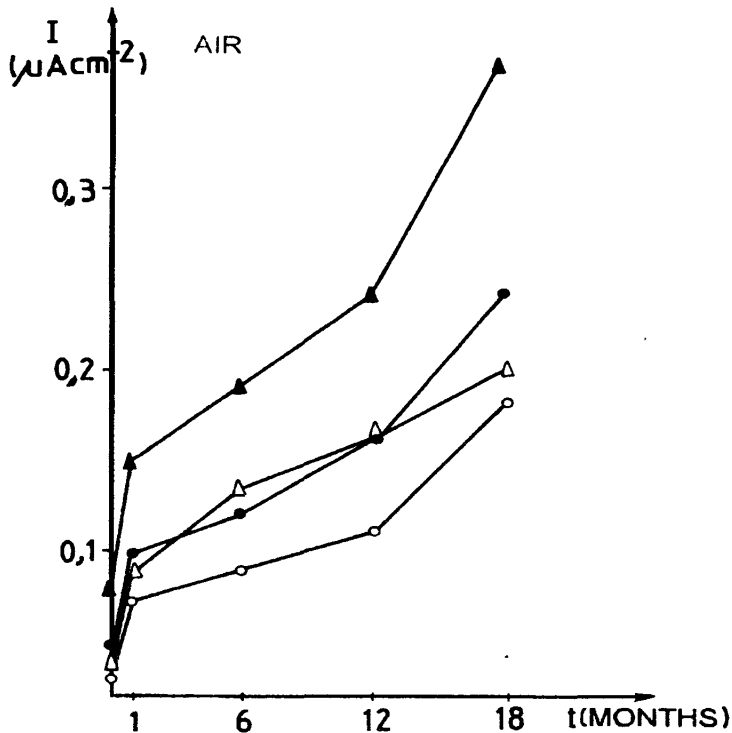


Fig. 3. - Dependence of tinplate corrosion on the time of storage in air: fill of peas (•), fill of string beans (\blacktriangle), 2.5 wt. % NaCl (\triangle) and 2.5 wt. % NaCl + 0.015 wt. % NaNO₃ (o)

The fills of peas have the highest corrodibility which is attributed to the physicochemical changes which occur during boiling, depending on the temperature and the chemical ingredients added to the solution in order to preserve a good appearance, texture and the green colour of chlorophyll. The increase of acidity, which is one of the reasons for the higher corrodibility of the fills, has been explained before.

If the negative charge of the pectine or of other macromolecules rises, their solubility decreases and thereby the adsorption of these molecules on the surface of the tins is prevented, so a protective film, which would prevent the corrosion upon of a tin, is not formed.

Cooling water usually contains 1 mg/dm³ of nitrates but, depending on the soil on which the plant has grown, the total amount of nitrogen compounds in the fills may be even greater, and thereby the corrodibility of the fills of string beans increases.

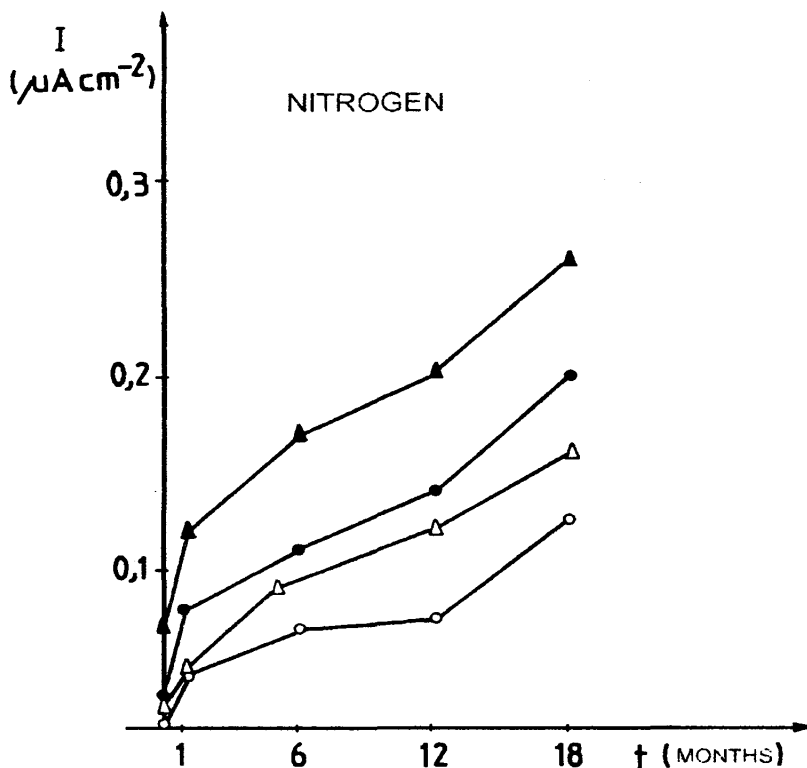


Fig. 4.- Dependence of tinplate corrosion on the time of storage in nitrogen stream: fill of peas (●), fill of string beans (▲), 2.5 wt. % NaCl (Δ) and 2.5 wt. % NaCl + 0.015 wt. % NaNO₃ (○).

During the process of cooling peas some alkaline salt is usually added, while the fills have higher pH values, in order to preserve the green colour of peas and prevent its wrinkleness. After that the grains are rinsed and put into tins. The corrodibility of these fills is somewhat lower (Van Buren, 1969).

Table 3 present the corrosion potentials, which are the most negative in the peas fills.

Starting determinations in peas are more negative than in string beans, and likewise they are more negative in the NaCl solution than in the solution mixture of NaCl and NaNO₃, that is, in the solutions in which the oxidation state of NaNO₃ is most expressed.

More positive potentials in the fills of string beans can presumably be attributed to the presence of macromolecular compounds in the solution, which can be adsorbed on the surface of the tin at the beginning of the determination.

The corrosion currents increase during storage and are the highest in the fills of string beans (the lowest pH value), then follow the fills of peas and the solution NaCl, and the lowest are in the mixture of NaCl and NaNO₃, which means that nitrates have the inhibiting effects on the corrosion process in this case.

Tab. 3. - Currents, potentials and corrosion rates in model solutions of salts in liquid contents of peas and string beans tins

| Medium | Atmosphere | Storage time (in months) | | | | | | | | | | | | | | |
|--|------------|---|--------------------|--------------------------|---|--------------------|--------------------------|---|--------------------|--------------------------|---|--------------------|--------------------------|---|--------------------|--------------------------|
| | | 0 | | | 1 | | | 6 | | | 12 | | | 18 | | |
| | | i_{corr} ($\mu\text{Ac}/\text{m}^2$) | E_{corr} (mV) | V_{corr} (mm/year) | i_{corr} ($\mu\text{Ac}/\text{m}^2$) | E_{corr} (mV) | V_{corr} (mm/year) | i_{corr} ($\mu\text{Ac}/\text{m}^2$) | E_{corr} (mV) | V_{corr} (mm/year) | i_{corr} ($\mu\text{Ac}/\text{m}^2$) | E_{corr} (mV) | V_{corr} (mm/year) | i_{corr} ($\mu\text{Ac}/\text{m}^2$) | E_{corr} (mV) | V_{corr} (mm/year) |
| Peas | in the air | 0.05 | -402 | 2.66· 10 ³ | 0.100 | -400 | 5.32· 10 ³ | 0.120 | -402 | 6.38· 10 ³ | 0.160 | -405 | 8.31· 10 ³ | 0.240 | -400 | 1.27· 10 ² |
| | nitrogen | 0.035 | -404 | 1.85· 10 ³ | 0.080 | -405 | 4.25· 10 ³ | 0.110 | -410 | 5.85· 10 ³ | 0.140 | -411 | 7.45· 10 ³ | 0.200 | -418 | 1.06· 10 ² |
| Beans | in the air | 0.080 | -380 | 4.25· 10 ³ | 0.150 | -395 | 7.98· 10 ³ | 0.190 | -390 | 6.38· 10 ³ | 0.240 | -398 | 1.27· 10 ² | 0.380 | -388 | 2.02· 10 ² |
| | nitrogen | 0.070 | -390 | 3.72· 10 ³ | 0.120 | -410 | 6.38· 10 ³ | 0.170 | -405 | 9.02· 10 ² | 0.200 | -416 | 1.06· 10 ² | 0.200 | -402 | 1.06· 10 ² |
| 2.5% NaCl | in the air | 0.040 | -400 | 2.12· 10 ³ | 0.900 | -395 | 4.79· 10 ³ | 0.135 | -390 | 7.18· 10 ³ | 0.160 | -398 | 8.52· 10 ³ | 0.200 | -306 | 1.06· 10 ² |
| | nitrogen | 0.030 | -395 | 1.59· 10 ³ | 0.050 | -400 | 2.66· 10 ³ | 0.090 | -405 | 4.79· 10 ³ | 0.120 | -401 | 6.39· 10 ³ | 0.140 | -407 | 7.45· 10 ³ |
| 2.5% NaCl + 0.015% NaNO ₃ | in the air | 0.030 | -305 | 1.59· 10 ³ | 0.075 | -302 | 3.99· 10 ³ | 0.090 | -308 | 4.79· 10 ³ | 0.110 | -318 | 5.85· 10 ³ | 0.180 | -340 | 9.50· 10 ³ |
| | nitrogen | 0.020 | -350 | 1.05· 10 ³ | 0.045 | -390 | 2.39· 10 ³ | 0.068 | -385 | 3.62· 10 ² | 0.075 | -360 | 3.99· 10 ³ | 0.125 | -348 | 6.60· 10 ³ |

Higher corrosion currents which produce higher corrosion rates, calculated by the equation 1 are shown in Table 3.

Conclusion

On the basis of the conducted analyses of the exchange of parameters during the storage and in model solutions and liquid contents (fills) of tins of peas and string beans, it can be concluded that the corrosion process is affected by the components found in the tinned foodstuff as well as by the additives added during production process. Likewise, these processes are more evident in tins during storage than at the beginning of determination.

Corrosion currents and thereby corrosion rates of tinplate, too, have higher values in tin fills than those defined in clean model solutions. The corrodibility decreases in the following order: string beans fill - peas fill - NaCl solutions - NaCl and NaNO₃ solutions.

Corrosion currents decrease noticeably in nitrogen atmosphere that spears in favour of package of foodstuff in inert atmosphere.

The obtained - calculated values of the corrosion rate show that during storage - preservation for the period of 18 months, the rate of corrosion of nonlacquered tins has the values of 10⁻² and 10⁻³ mm/year, which is considerably less than the allowed (MAC - *Maximum Allowable Concentration*) value of 0.12 mm/year, for inlacquered tins. Thus, it is assumed that tins made of tinplate manufactured in the factory for tinplate production, "Sartid 1913" d.d. at Šabac, and the tins of

commercial production were made of ("Limprodukt", Novi Sad), filled with peas and string beans can be safe for foodstuff preserving during the time period of several years.

REFERENCES

1. Gerischer, H., Tobias, W.C. ed. (1978): *Advances in Electrochemistry and Electrochemical Engineering*, Vol. II, John Wiley & Sons, New York, pp. 273-352.
2. Alby-Yaron, A., Berthelin, N., Chisten, J.M., Pagetty, J. (1979): A Tentative Evaluation of the Potentiocinetic Polarization Technique in Studies of Localized Corrosion of Lacquered Tinplate, *J. Food Technol.*, Vol. 14, pp. 9-19.
3. Butler, T.J., Carter, P.R. (1963): A Polarization for Determining the Corrosion Rate of Tinplate, *Electrochem. Technol.*, Vol. 1(1-1), pp. 22-27.
4. Catala, R., Cabanes, J.M. (1981): Aplicacion de Technicas Electroquimicas Para el Estudio de los Problemas de Corrosion de los Envases de Hojalata, *Rev. Agroquim. Tecnol. Aliment.*, Vol. 21 (3), pp. 341-352.
5. Dražić, D.M., Vaščić, V. (1985): *Hemijska industrija*, 39, s. 1.
6. Kamm, G.G., Willey, A.R. (1961): *Corrosion*, Vol. 17, p. 99.
7. Mansfeld, F., Jean, S.L., Kending, M.W. (1986): *Corrosion Sci.*, Vol. 26, p. 735.
8. Nagy, S., Rousffe, R., Sik-Vune (1980): *J. Agric. Food. Chem.*, Vol. 28, pp. 1166-1169.
9. Niketić-Aleksić, G. (1994): Tehnologija voća i povrća, Poljoprivredni fakultet, Beograd-Zemun.
10. Oldhem, K.B., Mansfeld, F. (1971): *Corrosion*, Vol. 27, p. 434.
11. Priručnik za liniju za elektrokalažisanje, United Steel Corporation, 1970.
12. Tošković, D., Rajković, M.B., Lačnjevac, Č. (1999a): Određivanje korozionih svojstava nelakiranog belog lima elektrohemijском polarizacionom metodom radi njegove primene u prehrambenoj industriji. Deo 1. Merenje korozionih svojstava limenki napunjenih pasterizovanom višnjom i kašom kajsije, *Zaštita materijala*, 40(2), s. 13-18.
13. Tošković, D., Rajković, M.B., Lačnjevac, Č. (1999b): Određivanje korozionih svojstava nelakiranog belog lima elektrohemijском polarizacionom metodom. Deo 2. Merenje korozionih svojstava konzervi napunjenih pasterizovanom polutkom šljive i sterilisanim graškom, *Zaštita materijala*, 40(3), s. 1-4.
14. Tsurumaru, M., Nunokawa, A., Suzuki, Y. (1980): Evaluation of Iron Exposure on Tinplate and Tinplate Cans, 2nd Internat. Tinplate Conf., London. 06.-10. Oct. 1980, pp. 348-359.
15. Trassati, S. (1971): *J. Electroanal. Chem.*, Vol. 33, p. 351.
16. Van Buren, J. (1969): *Food Technol.*, Vol. 23(6), pp. 92-94.
17. Van Vliet, T., Wolstra, P. (1980): *J. Texture Studies*, Vol. 11(1), p. 65.

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ODREĐIVANJE BRZINE KOROZIJE U KONZERVAMA NAPUNJENIM GRAŠKOM I BORANIJOM ZA VREME SKLADIŠTENJA

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Rezime

U radu su dati rezultati ispitivanja korozionog ponašanja elektrolitičkog belog lima u model rastvorima soli i tečnom sadržaju (nalivu) konzervi graška i boranije. Na osnovu urađenih ispitivanja promene parametara tokom skladištenja a u model rastvorima i tečnim sadržajima (nalivima) konzervi graška i boranije, može se zaključiti da na proces korozije imaju uticaj komponente koje se nalaze u namirnicama koje su konzervirane, a isto tako i dodaci koji se dodaju u toku procesa proizvodnje. Takođe, ovi procesi su u konzervama više izraženi za vreme skladištenja nego na početku određivanja.

Struje korozije, a samim tim i brzine korozije belog lima, imaju više vrednosti u nalivima konzervi od onih koje su određene u čistim model rastvorima. Korozivnost opada u sledećem nizu: naliv boranije - naliv graška - rastvor NaCl - rastvor NaCl i NaNO₃.

Struje korozije se osetno smanjuju u atmosferi azota, što govori u prilog upotrebe pakovanja namirnice u inertnoj atmosferi.

Dobijene - izračunate vrednosti brzine korozije pokazuju da je tokom skladištenja - stajanja 18 meseci brzina korozije nelakiranih konzervi reda veličine 10⁻² i 10⁻³ mm/god, što je značajno manje od dopuštene (MDK) vrednosti od 0,12 mm/god, za lakirane konzerve. Na taj način, predpostavlja se da konzerve proizvedene od belog lima iz domaćih fabrika mogu biti bezbedne za čuvanje namirnica tokom višegodišnjeg vremenskog perioda.

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