Evaluation of Adherence and Performance of Epoxyphenolic Coatings on Electrolytic Tinplates

E. Zumelzu[a*] and F. Rull[b]

[a]*Universidad Austral de Chile, Casilla 567 - Valdivia, Chile*
[b]*Departamento de Física de la Materia Condensada, Cristalografía y Mineralogía*
Universidad de Valladolid, 47006, Valladolid, España.

ABSTRACT

The adherence of epoxyphenolic coatings on electrolytic tinplates through mechanical-electrochemical trials, determination of the contact angle (CA) and work of adhesion was studied. The performance and degradation of the coated tinplate was evaluated by polarization tests and Attenuated Total Reflection (ATR) vibration spectroscopy. The micro- and ultra-structural characterization of the epoxy-phenolic films was made by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The results showed that the existence of pores and surface defects influenced the quality of the adherence of the coating and that the citric-citrate solution does not degrade this type of sanitary lacquer under the tested conditions.

Keywords: Adherence, performance, tinplate, epoxyphenolic coating, and characterization.

INTRODUCTION

Tinplate is still present in large amounts in the food market due to technological factors and lower costs when compared to other materials (e.g., aluminum) /1-3/. Current improvements in the development of new products include reduction in weight, competition between manufacturers, and higher consistency of the mechanical properties in order to guarantee the automation of processes, quality and resistance to corrosion, and price ranges, among others /4/.

Tinplate is a composite material, since it has a stratified structure /5/ formed by wrought iron which provides mechanical strength, an $FeSn_2$ alloy layer resulting from the brightening process that protects the steel from the galvanic corrosion of oxidant species, a free tin layer which extends the useful life of materials and formation of cans by acting as sacrificial anode, and chrome, tin, and metal chrome oxides, which prevent the development of tin oxides and the sulfuring process in food cans.

Food cans are made of tinplates coated with a sanitary lacquer as a protection layer, which acts against corrosion by the media. Epoxyphenolic coatings are widely used in multiple applications.

The aim of the present work is to characterize and evaluate the adherence of epoxyphenolic coatings on electrolytic tinplates, by means of a combined mechanical-electrochemical test, which substitutes the standard T-peel trial. In this sense, this test relates different variables, such as the contact angle between the coating and tinplate, adherence work, and microstructure with the quality of adherence. In addition, it is our purpose to evaluate the performance of the epoxyphenolic coating against a cathodic attack and to analyze possible structural changes or degradation of the protection polymer by ATR vibration spectroscopy techniques. In order to characterize the

---

[*] Ernesto Zumelzu, Director Instituto de Materiales y Procesos Termomecánicos, Universidad Austral de Chile, Casilla 567, Valdivia, Chile. Email: ezumelzu@uach-cl, Fono: 56-63-221863. Fax: 56-63-221033.

epoxyphenolic coating and its performance when applied to tinplate, electron microscopy techniques such as SEM and TEM are employed.

This study will hopefully clarify the corrosion problems of tinplate, since it is essential to be aware of the protection role of the epoxyphenolic coating, because its application creates a change in the nature of the physicochemical interactions between the can and the food product.

MATERIALS AND METHODS

The characteristics of the electrolytic tinplates and those of the coating employed are indicated in Tables 1 and 2.

The electrolytic tinplate used in the containers under study is of the type E-1/2 manufactured by continuous casting and annealing, as described in Table 1.

Table 1

Characteristics of continuous casting and annealed tinplates.

Parameter	Amount
Thickness (mm)	0.23
Hardness (Rc)	57.60
Tin weight (g/m^2)	
• Upper layer	6.63
• Lower layer	3.78
Alloy layer (g/m^2)	
• Upper layer	1.31
• Lower layer	1.20
D.O.S. Oil (mg/m^2)	
Coating (g/m^2)	
Gold lacquer	1.30

Commercial organic coatings applied on tinplate were of the epoxy-phenolic type, an essential component to promote adhesion, film strength, flexibility, chemical and corrosion resistance.

The average composition of epoxyphenolic tinplates normally is 34% dry extract, 66% solvents (metal – isobutyl – ketone, butanol, xylol, and butylenglycol), and acid catalysts of reticulation such as phosphoric acid.

Table 2

Characteristics of type of coating used.

Coatings Type	Gold epoxy-phenolic
Viscosity (seconds 4 Ford Cup at 77°F)	100
Specific gravity (g/cm^3)	0.961
Percentage of solids (%)	35.5
Ignition point (°F)	75

The adhesion implies the union of two surfaces; therefore, it is necessary to determine the surface characteristics of the joining materials. A necessary condition for the adhesion to occur is that the substrate be moisturized by the adhesive, so that a large number of contact points take place on both surfaces at the interface.

The CA contact angle measurements are widely used, especially for comparison purposes, in the evaluation of the degree of rugosity / surface heterogeneity of materials, but mainly in order to determine the surface energy of the solids.

For the determination and analysis of the CA contact angle of the epoxyphenolic lacquer with the tin, samples of bad adherence pre-evaluated in trials at the plant were included, in order to compare the resulting values.

The static AC was measured in a goniometric system /6/, that basically consists of a thermostatized glass chamber in which the solid is deposited. The quantification of the AC was obtained by a direct method, through the projection of the tangent and measurement of the corresponding angle.

The combined electrochemical-mechanical trial was employed to evaluate the adhesion of the coating to the tinplate. This test revealed and quantified the weak areas of tinplate/polymer-coating adhesion. This method is better suited than the T-peel test /7/, because the effective force required to separate this type of lacquer from the tin is very difficult to quantify due to the reduced thickness of the coatings /8/.

The above-mentioned combined method is a wet-adhesion procedure accomplished by the potentiostatic polarization of the lacquer-coated sample at -200 mV/SCE for 30 min in a citric acid solution buffer at pH = 3.01 M. This treatment induces undermining by corrosion products and hydrolysis of the coating, simulating the service conditions of a container or final product, providing an idea of the chemical stability of the interface and of the effect of its degradation on the adhesion of the co-rolled coating. At the end of this treatment, the surface is washed, dried and the polymer coating is mechanically separated using an adhesive tape.

Later, the naked area resulting from the mechanical detachment is measured by means of a microscope and a reticulated pattern. The results are expressed as a percentage of the adhered coating, that is to say, the relationship between the attached and total area.

A simulated polarization or constant over-potential test of the samples was done in order to characterize the chemical and structural changes on the protection films and to evaluate an eventual degradation of the polymer coatings by ATR spectroscopy,

The methodology /8,9/ employed consisted of placing 16-mm diameter disks on a sample-holder. Then, an electrochemical cell was filled with 120 ml of electrolyte, and the working electrodes, Luggin capillaries, a platinum counterelectrode, and the tubes for the nitrogen bubbling were introduced in the cell.

This was an anodic polarization trial of the tin samples, performed at +10 mV, for a period of 30 minutes, to take them out of their balance condition and to recognize when the system attempts to accommodate to the new situation, which is detected when a constant current is achieved.

The thirty minutes of this trial were not intended to obtain a constant current, but to achieve a significant degradation of the solid that can be measured by both spectrometry and electron microscopy. The 10 mV were used to achieve the lowest interference possible, so that the behavior was the most similar to the balance seen at the interface.

The structural characterization and degradation of the epoxyphenolic coating in the various trials performed was carried out by SEM and TEM using ultra-thin cuts in the order of 600 Å.

The ATR (Attenuated Total Reflection spectroscopy) technique was employed to characterize the spectra of the coatings on the tinplates. The ATR method is particularly useful in the analysis of thin layers or films on substrates, since the penetration of the infrared radiation on the material is in the order of a few microns.

The size of the samples used was 1 x 3 cm and 1 x 5 cm for the composition and structural analyses. Longitudinal and cross-sectional analyses were performed to detect the extension of eventual degradations on the coatings during the simulated polarization trials, combining the specific characteristics of each one of the techniques.

Spectra obtained directly from the tinplates were used for comparison purposes with isolated epoxyphenolic-coated control samples.

RESULTS AND DISCUSSION

The EDAX surface microanalysis of the tinplate is shown in Figure 1, where Sn, Fe, Mn, and Cr are evident.

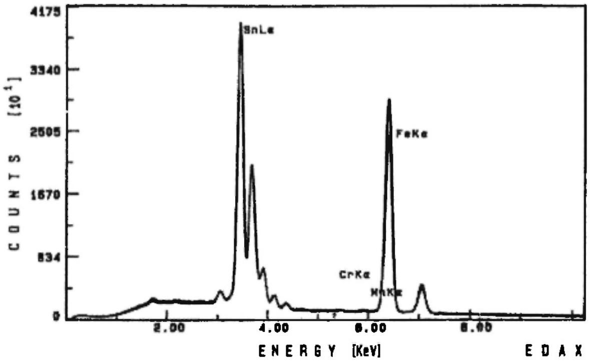

Fig. 1: EDAX microanalysis of tinplate.

The results for the three coupons of the same material in the combined electrochemical-mechanical trials of adherence are described in Figure 2.

During the first stage, excessive amounts of electrons are captured by the protons present in the dissolution, which is followed by a release of gaseous hydrogen. This is an important fact, since an electronically active medium must exist for the reaction to take place. This medium can be the metal exposed in the pores of the polymer film or even polymer areas that may become conductors.

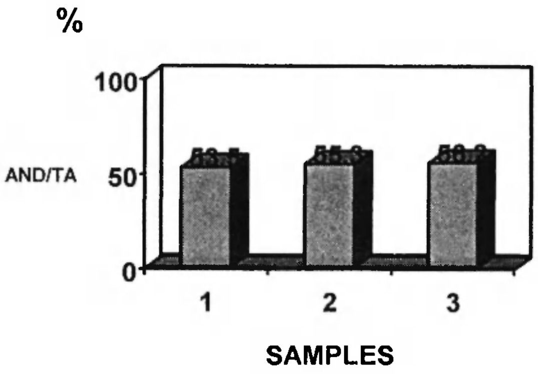

Fig. 2: Percentage area not detached and with respect to total area of coating in the mechanical-electrochemical adherence trial.

With this test, porosity and adherence occur at the same time. The porosity arises as a result of the current generated by the contact between the electrolyte and the metal surface. On the other hand, during the adherence process, the gas resulting from the cathodic process exerts a pressure that eventually leads to polymer detachment. The action of the gas takes place mainly adjacent to or outlying to the pore.

When observing the samples by scanning electron microscopy (SEM) after the combined trial, significant areas of epoxyphenolic lacquer detachment were evident as seen in Figures 3 and 4.

Table 3 summarizes the CA's for the coating and tinplate, and the adhesion work values (W_A) calculated at time zero and after thirty minutes.

Once the CA is known, it is possible to theoretically determine the adhesion work or surface energy of the coating through the following equation:

$$W_A = \gamma_{LV}(1+\cos\theta)$$

where, W_A is the adhesion work, γ_{LV} is the surface tension of the liquid (in this case water, with a value of 72.8 mN/m) and CA.

The CA measurements after 30 minutes allowed evaluating its runoff behavior. If the drop had not expanded or, what comes to the same thing, if the drop had not wet the surface, no adhesion would have occurred.

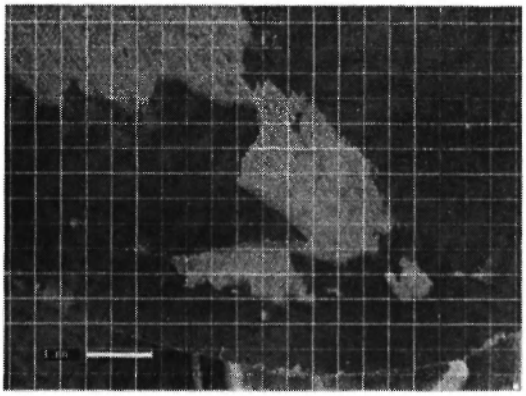

Fig. 3: Detachment of epoxyphenolic lacquer (light zones) by the action of adhesive tape after electrochemical attack (SEM, x 100).

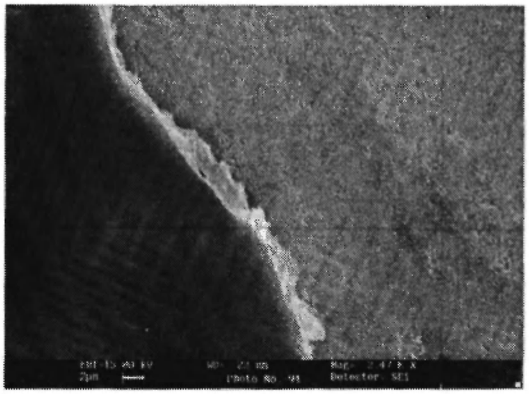

Fig. 4: Detail of detached area and epoxyphenolic lacquer fracture. The fracture is irregular in shape and the tinplate surface is continuous after electrochemical attack (SEM, x 100).

From Table 3 it can be seen that the measurements of the contact angles provided the expected values, lower than 90 degrees, which allowed adequate surface tensions between the metal and the organic parts. The former was supported by the combined electrochemical-mechanical trial, since the exposed surfaces were as predicted for the epoxyphenolic coatings and no evidence of significant detachment was observed for the passivation and free-tin layer.

Table 3
CA and adhesion work values of epoxyphenolic coatings on tinplates (TP).

Coating	AC (degrees)		Adhesion work W_A (m N/m)	
	t = 0	t = 30'	t = 0	t =30'
Epoxyphenolic on TP, poor adherence	90	70	72.8	97.82
Epoxyphenolic on TP, good adherence	81	58	84.3	111.61

On the other hand, the results of the samples attacked by the anodic trial to evaluate the structural changes or degradation of the epoxyphenolic lacquer on the tinplate showed that a sample of good adherence is much less reactive than a control sample of bad adherence, considering that the current values differ in a factor of 1,000. Since the current in the sample of good adherence is low, it does not require such a long time to reach certain stabilization; on the contrary, it is almost instantaneous.

The controlled lacquer damage trial, for later analysis by ATR, showed evidence of pores and surface defects on the coating. However, the ATR vibration spectroscopy (Figs. 5 and 6) results showed no new bands originating chemical changes on the epoxyphenolic coating.

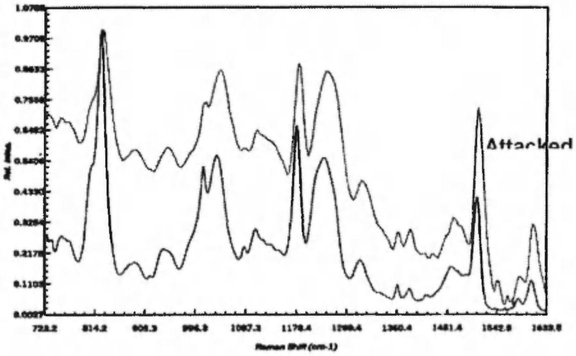

Fig. 5: ATR spectrum analysis of good adherence lacquered tinplates with and without undergoing the electrochemical trial.

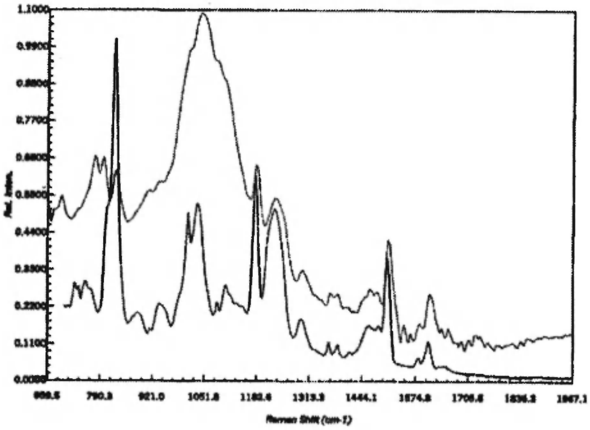

Fig. 6: ATR spectrum analysis of poor adherence lacquered tinplates with and without undergoing the electrochemical trial.

The TEM characterization of epoxyphenolic coatings on samples not submitted to previous electrochemical trials showed an amorphous morphology and the existence of pores, which facilitate the electrolyte-tinplate interaction in food-can applications, Figure 7.

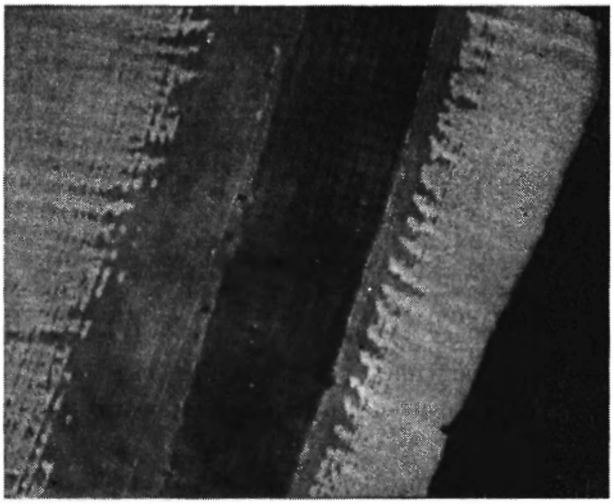

Fig. 7: Ultrathin cut of epoxyphenolic coating showing zone of pores that influences the lacquer permeability and resistance to electrolyte attack. The lack of continuity facilitates delamination and failure of coating adherence (TEM x 2,400).

Figure 8 show the microstructure of the epoxyphenolic films by TEM after the electrochemical attack, and the performance of the coating by the electrolyte action. Metal traces migrating to the electrolyte through the pores caused by the electrochemical reactions during the anodic trial are evident.

Fig. 8: Ultrathin cut of epoxyphenolic coating (gray) on tinplate, after electrochemical trial. Small oxide particles, 40-200 nm in size, are trapped in the lacquer because of the accelerated electrochemical trial to detach the coating (TEM x 24,000).

It is well stated that the adhesion depends on the chemical surface and physical nature of the polymer coating and metal substrate, as well as the interactions between them at the interface level. The presence of polar or polarizable functional groups on the polymer or coating surface, such as -C≡N, -C-O-H, -C=O, -C-OOH, with an acid or base character, play a fundamental role in obtaining a good adherence. Some authors /10/ have proved that donor electrons or acceptor sites with an acid or base character are present on the thin surfaces of oxide films showing chemical heterogeneity, such as non-stoichiometric oxides /10/ and different oxides with semiconducting properties.

CONCLUSIONS

Under the experimental and technical conditions of the present work, the following conclusions can be drawn:

1. The stratified structure confers the tinplate a set of properties and capabilities in order to protect the base steel, favor the adherence to coatings, and provide corrosion resistance, where each substrate is capable of accomplishing a specific function.
2. Concerning the capacity of polymer coatings of acting as a protection barrier, it was shown that the existence of pores affects the adherence on tinplates and the resistance to microcorrosion. A high density of pores allows an interaction with the metal at the interface level, leading to ionic dissolution of the tinplate's components.
3. Our electron microscopy and vibration spectroscopy studies showed that the epoxyphenolic coatings on tinplates have an amorphous structure, with pores and surface discontinuities that limit the adherence of materials.

   The ultrastructural studies on the epoxyphenolic coatings showed that they contain metal components trapped in their structure as a result of electrochemical attacks, migration of ions, contamination, or eventually as a consequence of their application on the surface of tinplates.
4. The ATR spectroscopy studies showed that there were no structural or chemical changes resulting from the electrochemical attack to the epoxyphenolic coating of the electrolytic tinplate.
5. The coating and its application procedure provide an adequate surface protection to tinplates in the canning manufacturing. The structural characteristics and morphology of coatings are in agreement with the well-known fact that they maintain their original properties after application to tinplate surfaces and following the mechanical and chemical adherence, and under the temperature and time conditions of this trial.

ACKNOWLEDGMENTS

To Conicyt-Chile for the financial support of the Fondecyt Project N° 1010180.

REFERENCES

1. P. Rogers. "The Future of Tinplate", *7th Int. Tinplate Conf., I.T.R.I*, Amsterdam, The Netherlands, 2000; 1-7.
2. J. Granboulan. "Prospects for the World Steel Packaging Market", *7th Int. Tinplate Conf., I.T.R.I*, Amsterdam. The Netherlands, 2000; 17-26.
3. E. Zumelzu, A. Vera and C. Cabezas, "SEM Analysis of Corrosion Degradation on Tinplate Substrates", *12th European Congress on Electron Microscopy*, Eurem 2000, (3) I 227-228, Brno, Rep. Checa, 2000.
4. R. Bulthe. *Research Strategy for Flat Rolled Products*, Prof. J. Dilewijins (Ed.), Universiteit Gent, Belgium, 1997; pp. 15-32.
5. E. Zumelzu and C. Cabezas. "Observations on influence of microstructure on electrolytic tinplate corrosion", *Materials Characterization*, **34**(2), 143-148 (1995).
6. J.M. Martin. "*Adhesion y Uniones Adhesivas*". Ed. Universidad de Alicante, Red Cyted VIII -D, España, 1998.
7. E. Zumelzu and G. Gipoulou. "A T-peel test to asses the adhesive properties of organic coatings applied to electrolitic tinplate", *Surface Coatings International, Part B*, **85** (B1), 35-38 (2002).
8. E. Zumelzu and C. Cabezas. "Influence of tinplate structure on its electrochemical perfomance in a citric-citrate medium", *Journal of Scientific & Industrial Research*, **55**, 274-276 (1996).
9. R. Catala and J.M. Cabañes. "Aplicación de técnicas electroquímicas para el estudio de los problemas de corrosion de los envases de hojalatas", *Revista Agroquímica y Tecnología de Alimentos*, España, **21**(3) 341-356 (1981).
10. G. Ingo, L. Giorgi and N. Azzerri. "Electrochemical and XPS Studies on Lacquer-Low Tinplated Adhesion", Corrosion Science, 33(3), 361-377 (1992).