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Technical Report

Chromate-free Tinplate (EZP™)

Shintaro YAMANAKA* Hirokazu YOKOYA
Yasuhiko SATO Toshiaki TAKAMIYA

Abstract

For metal packaging application, Electrolytic Tinplate (ETP) has been used globally for a long time with its excellent performances as packaging material and its food safety as food contact substances. Since the passivation film on ETP for packaging contains Cr (III), not Cr (VI), it is considered to be safe and there have been no food safety issues with ETP. However, in order to further improve occupational safety (health-related concerns in working environments) in tinplate production processes, new technology that will not use Cr (VI)-containing chemicals has been developed by Nippon Steel Corporation. This is a new chromate-free passivation treatment technology named EZP™, which uses Zr-containing chemicals, instead of Cr (VI)-containing chemicals. This report on EZP™ technology will cover the main technical information about the product and food contact safety of EZP™ tinplate.

1. Introduction

Tinplate is a steel sheet product coated with tin, and is used worldwide mainly as a material for containers, such as food can, beverage can, general can and so on. Tinplate is an infinitely recyclable material and can be easily recycled; its recycling rate in Japan exceeds 90%. In addition to having the basic properties of a container material such as lacquer adhesion, resistance to sulphide staining, corrosion resistance and compatibility with aesthetic design, tinplate is required to be safe as a material that is contact with food. For the purpose of maintaining and improving these requirements, the surface of tinplate is generally coated with passivation films, typically such as chromate passivation film. While chemicals containing hexavalent chromium were traditionally used for the chromate passivation treatment process, the passivation film itself consists of trivalent chromium and was considered safe as a food contacting material, and there was no safety problem. However, it has been decided in Europe that the use of hexavalent chromium for the chromate passivation treatment process will be prohibited under the REACH regulation for the improvement of the working environment (scheduled to come into effect in April 2024). Taking into consideration such environmental movement in the EU and requests for supply of chromate-free tinplate from consumers and related fields of industry, Nippon Steel Corporation has developed a new chromate-free tinplate product, EZP™, with a new passivation film free of substances containing chromium.[1, 2)]

2. Overview of Chromate Free Tinplate, EZP™

The tin layer of the developed chromate-free tinplate, EZP™, is coated with an inorganic chemical film containing zirconium oxide, instead of the conventional chromate passivation film; **Fig. 1** schematically shows the coating structure of EZP™. The new passivation film is capable of replacing the conventional one thanks to the barrier function and chemical stability equal to those of the chromate passivation film. In addition, the new passivation film can be quickly formed on the tin plating layer, like the chromate passivation film, by cathode electrolysis in an aqueous solution. For this reason, it is possible to control the amount of the zirconium oxide according to the final use and required performance by appropriately regulating the electrolysis process, and it is also possible to measure the coating weight inline; this new passivation process is excellent for continuous industrial production at high speed.

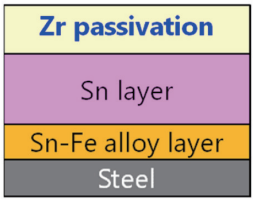

Fig. 1 Schematic illustration of chromate-free tinplate (EZP™)

* Senior Manager, Head of Section, Senior Researcher, Surface Treatment Research Section, High-performance Steel Sheet Research Dept., Kyushu R & D Lab. 1-1 Tobihata-cho, Tobata-ku, Kitakyushu City, Fukuoka Pref. 804-8501

3. Examples of Characteristics of EZP™

Some of the basic characteristics of EZP™ are presented below.

3.1 Lacquer adhesion

When tinplate is used as a container, its inner and outer surfaces are usually coated to enhance resistance to corrosion and sulphide staining, and compatibility with aesthetic design, etc., in consideration of the contents and use. To this end, lacquer adhesion is one of the important functional items required for container materials. The lacquer adhesion of EZP™ was evaluated in the following manner: using a bar coater, a commercially available polyester lacquer, BPA-NI, was applied to the surfaces of EZP™ specimens and comparative specimens with conventional chromate passivation films, and the specimens were subjected to the crosscut test according to JIS K 5600-5-6, before and after retort treatment. In the retort treatment, which was conducted at 121°C for 60 min, three different solutions, namely, 3% saline, 1.5% acetic acid, and 1% citric acid + 1% saline, were used as food simulating solutions. **Photo 1** shows the appearances of the specimens after the test. No peeling of the lacquer film was observed with the EZP™ specimens, either before or after the retort treatment with any of the food simulating solutions, which confirmed good lacquer adhesion of the developed product.

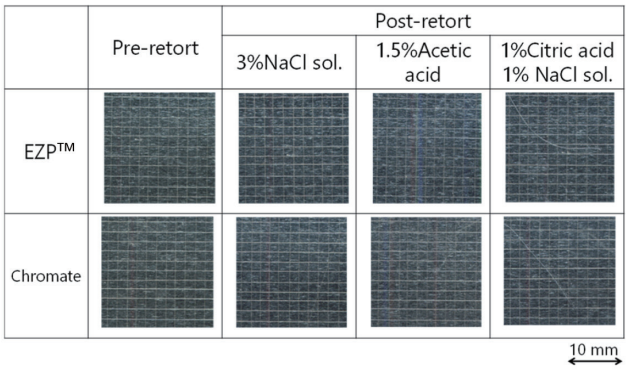

Photo 1 Appearance of samples after lacquer adhesion test (BPA-NI lacquered)

3.2 Resistance to sulphide staining

When tinplate is used as the material of food cans for contents containing protein such as fish meat, beef, beans, the inner surface of the can may turn black. This is called sulphide staining, and is caused by the reaction of hydrogen sulphide, which is formed owing to the decomposition of some protein during retort treatment, with tin and iron to form black sulphide. Sulphide staining does not impair the flavor of the contents and is not a problem for food safety, but it impairs the appearance of the food, and is undesirable for consumers; thus, resistance to sulphide staining is one of the basic requirements for tinplate. The sulphide staining resistance of EZP™ was evaluated in the following manner: specimens of EZP™, chromate passivated tinplate, and tinplate without the passivation film were coated with the same polyester-based lacquer as in Subsection 3.1 above using a bar coater, retorted in a 0.6% cysteine aqueous solution at 125°C for 60 min, and staining or otherwise of the specimen surfaces was visually evaluated after the retorting. **Photo 2** shows the appearances of the specimens after the retort treatment. Whereas the surface of the specimens without passivation turned black, no such staining was observed with EZP™, confirming its good sulphide staining resistance, the same as that of the chromate passivated tinplate.

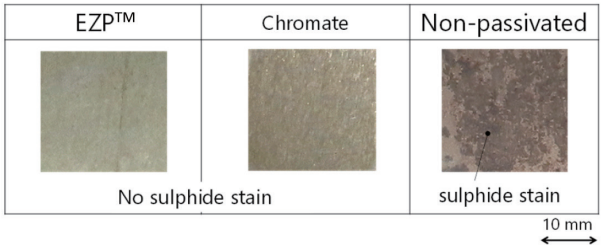

Photo 2 Appearance of samples after sulphide stain test (BPA-NI lacquered)

3.3 Heat resistance

When tinplate is used for food cans, it is often heated directly by burners to sterilize the can inside before filling them with the contents. When used for three-piece cans, it is affected by welding heat in the portions near the weld seam. To maintain the basic performance items of food containers such as the lacquer adhesion and resistance to sulphide staining in these parts, it is desirable that the passivation film has heat resistance so that it stably survives the welding heat. In addition, when a newly developed tinplate product such as EZP™ is used for food containers for the first time, it is necessary to obtain approval for its use as a food contact material in the country or region where it is used. If the structure of the tinplate changes as a result of decomposition of the passivation film owing to heat, food safety may not be approved. In consideration of this, the passivation film structure near the continuous seam weld was investigated by X-ray photoelectron spectroscopy (XPS) as part of the examination of the heat resistance of EZP™. **Figure 2** shows narrow scan profiles of $Zr3d_{5/2}$. Peaks were observed at the binding energy positions corresponding to zirconium oxide (ZrO_2) both in a heat-affected zone and a normal portion, which confirmed that the zirconium oxide film existed stably even in the heat-affected zone.

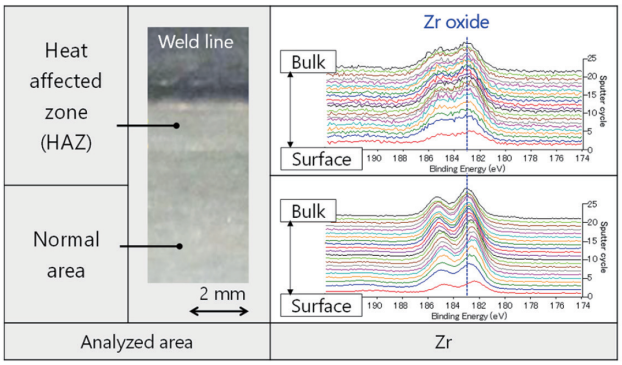

Fig. 2 XPS narrow scan profiles near welded area (surface–bulk)

3.4 Corrosion resistance (storage test of real food cans)

Cans made of EZP™ were filled with real food and kept for long periods to evaluate the corrosion resistance of the product. Three-piece cans, each composed of an easy open end (EOE), a body, and a normal end, were made through a commercial can production line, using either EZP™ or conventional chromate-passivated tinplate for all the parts, and after being filled with light colored fruits through a commercial canning line, they were stored at room temperature in a warehouse at Nippon Steel's Kyushu Works. The amount of tin that

eluted in the content syrup was measured by using induced coupled plasma (ICP) at intervals of six months for more than three years. The state of tin corrosion (detinning) at the inner can surface was also observed. The inner surface of the EOE was coated and the adhesion of the lacquer film was examined by the cross cut test. **Figure 3** schematically shows a stored sample can and its contents.

Figure 4 shows the change in the amount of tin eluted in the content syrup. The change in the tin elution in the syrup of the EZP™ during the period from the 36th month, the best before limit, to the 40th was substantially the same as that of the cans of the tinplate with chromate passivation; the good corrosion resistance of EZP™ has thus been confirmed. **Photo 3** shows the inside appearances of the bodies of the stored cans after 36 months of storage. There were tin crystals evenly distributed over the entire inner surface of the EZP™ can, like the one of the chromate passivated tinplate, which indicates that detinning occurred uniformly without local corrosion, and the sacrificial protection function was maintained satisfactorily.

Photo 4 shows the appearances of the inner surfaces of the EOE test pieces after the cross cut test after 36 months of storage. Peeling of the lacquer film was not observed either with the EZP™ specimen or with the tinplate specimen with chromate passivation films, which confirmed that the EZP™ had good lacquer adhesion in actual use in the real environment.

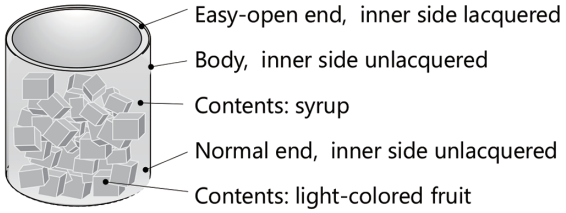

Fig. 3 Schematic illustration of samples for long-term storage test

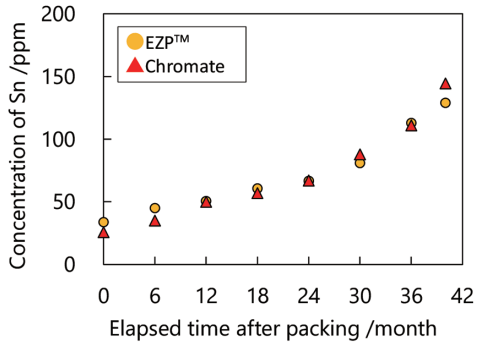

Fig. 4 Concentration of Sn in syrup

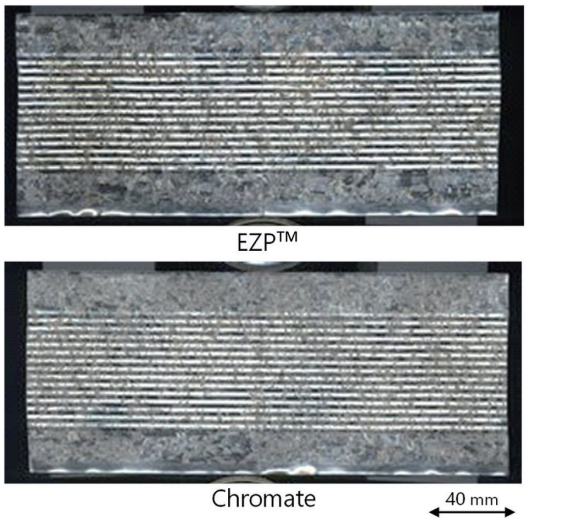

Photo 3 Appearance of inner side of can body after storage for 36 months in ambient atmosphere

4. Food Safety of EZP™

When a newly developed steel sheet product such as EZP™ is used as a material for food or beverage cans, it is imperative for it to be approved as a food contact material by the relevant authority of the country or region where it is used; this requirement is essential to the food container industry, quite different from the fields of automobiles, building construction, etc. Nippon Steel has worked to obtain the approval for EZP™ for a long time, and to date, it has been officially accredited as a food contact substance for its high safety in the USA (by the Food and Drug Administration) and European Union. Currently, the approval procedure in MERCOSUR (South American Common Market) is underway (see **Table 1**).

5. Conclusion

An outline of the new tinplate product coated with chromate-free passivation film, EZP™, its basic functions, and the main technical information on its food safety have been presented above. The developed product exhibits the same functions as those of conventional chromate passivated tinplate but is more environmentally friendly than the conventional one. Nippon Steel has started its commercial production on a full scale in 2020. Various can makers who are interested in it are proceeding with material evaluation, and its sales are expected to increase further in the near future.

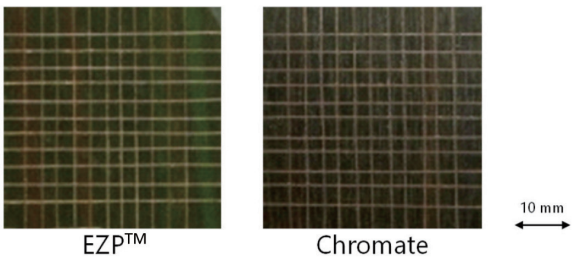

Photo 4 Appearance of inner side of easy open end of can after lacquer adhesion test (36 months of ambient storage)

Table 1 Official approval of EZP™ for food packaging material

Market	USA	EU	Mercosur/Brazil
Official approval	FDA/FCN 1253 Jun 8, 2013 (All food types & powdered IF) IF: Infant formula	EU/Dutch G4 Jan 12, 2016 (New SML for Zr: 2 mg-Zr/kg-food)	Mercosur /Brazil Anvisa (underway)
Certificate of compliance	Certificate given	Certificate given	Under examination

References

1) PRESS RELEASE 2021/10/20: at Nippon Steel Corporation's web site https://www.nipponsteel.com/news/20211020_200.html
2) Yamanaka, S., Sato, Y., Takamiya, T., Yokoya, H.: 12th International Tinplate Conference, 20–21st October 2021

Shintaro YAMANAKA
Senior Manager, Head of Section, Senior Researcher
Surface Treatment Research Section
High-performance Steel Sheet Research Dept.
Kyushu R & D Lab.
1-1 Tobihata-cho, Tobata-ku, Kitakyushu City,
Fukuoka Pref. 804-8501

Hirokazu YOKOYA
General Manager R&D
Tin Mill Product Planning Section
Tin Mill Technology Dept.
Tin Mill Products Div.
Kyushu Works

Yasuhiko SATO
Senior Manager
Tinplate Product Planning Section
Tinplate Quality Control Dept.
Quality Management Div.
Kyushu Works

Toshiaki TAKAMIYA
Chief Manager
Tin Mill Products Technology Dept.
Tin Mill Products & Electrical Steel Sheet Div.