

Development of Laminated Tin Free Steel (TFS) “UNIVERSAL BRITE®” Type F for Food Cans†

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Abstract:

JFE Steel has developed and commercialized a new PET-laminated tin free steel (TFS) sheet for food cans, “UNIVERSAL BRITE®” Type F, which satisfied the performance requirements for food cans and is also environment-friendly. As features, “UNIVERSAL BRITE®” Type F has an excellent balance of high formability and the content release property, which is required in food canning applications. An excellent content release property was realized by adding original surface-modifying additives to the polyethylene terephthalate (PET) film to reduce the surface free energy of the PET film. Formability is markedly improved by applying a combination of a new homopolymer PET (homo-PET) film with a unique structure and an original laminating technology which inhibits PET crystallization.

1. Introduction

From the viewpoint of protecting the global environment and improving the labor environment during painting work, in recent years, the can-making industry has avoided the use of organic solvents in painting, either by converting to water soluble lacquer or adopting thermoplastic resin laminated films as a substitute for paint. Against this background, cans produced from steel sheets laminated with a polyethylene terephthalate (PET) film have already been commercialized in the field of beverage cans¹⁾. As advantages of film-laminated steel sheets, because the painting/baking process required with conventional painted materials can be omitted, (1) costs are reduced by eliminating this

process and (2) use of organic solvents and other harmful substances can be eliminated. The PET-laminated steel sheets currently used in Japan also have various other outstanding features such as formability, corrosion resistance, and adhesion, and as a result, production has shown an increasing tendency in recent years. Based on these circumstances, JFE Steel successfully developed and commercialized a new laminated tin free steel sheet, “UNIVERSAL BRITE®” Type F, for food cans, which is environment-friendly and satisfies the performance requirements of food canning. This paper discusses the development concept and presents an outline of the technology which was newly established based on this concept.

2. Development Concept

The main properties required in food cans are the content release property, formability, and designability.

- (1) The content release property is a property which evaluates the ease of removing the contents packed in food cans, but could not be achieved with the existing PET-laminated steel sheets. A detailed study of this phenomenon revealed that the content release property depends on the separation property between the contents and the PET-laminated steel sheet, and the surface free energy of the PET-laminated steel sheet is the governing factor. Therefore, techniques for reducing the surface free energy of the PET-laminated steel sheet were investigated.
- (2) Formability is required so that the laminated steel sheet can follow deformation during forming with-

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out breaking or cracking. Although it is possible to produce draw-redraw (DRD) food cans using copolymer PET-laminated steel sheets²⁾, the high cost of the film (due to the high cost of the copolymer component) was a problem. Application of inexpensive homopolymer PET (homo-PET) film-laminated steel sheets is desirable as a solution to this problem, but because homo-PET films have an remarkably high crystallization kinetic in comparison with copolymer PET films³⁾, rapid crystal growth occurs during can-making due to the stress and heat generated by the bending and drawing processes. As a result, this material is unable to follow forming and could not be applied in can-making. JFE Steel therefore carried out an investigation focusing on techniques for inhibiting crystallization of the PET film, and studied application of a new type of homo-PET film⁴⁾ in which crystallization behavior is inhibited by reducing the mobility of the PET molecules. As a distinctive feature of this technique, the molecular structure of the PET is controlled so that some amorphous molecules form a quasi-bridge structure, thereby reducing their mobility.

- (3) In the external appearance of food cans, a color tone (metallic color, etc.) with a rich luster is required. For this reason, it is necessary to impart an appearance with a metallic color to laminated steel sheets for food cans by adding a colorant to the film. However, if heat treatment such as retort sterilization (125°C, 90 min) of the contents is performed, the colorant tends to lose its color due to migration/segregation to the film surface, deteriorating the design property. Therefore, a technique for inhibiting this phenomenon of heat-induced migration of the colorant was studied.

3. Experimental Method

3.1 Specimens

The substrate used for film lamination was a tin free steel (TFS) of low carbon aluminum-killed continuously-cast steel (Temper degree: T3CA, Thickness: 0.24 mm) with a metallic chrome coating weight of 120 mg/m² and chrome hydrate oxide coating weight of 15 mg/m² (as Cr content). Surface free energy was adjusted by laminating a new type of biaxially-oriented homo-PET film (Thickness: 15 μm), to which various types of surface-modifying additives had been added, to the surface of the TFS. Lamination was performed by thermal bonding after heating the TFS to 200–280°C. The cross-sectional structure of the PET-laminated TFS is shown in **Fig. 1**. As comparison materials, various types of painted materials and olefin film-laminated steel sheets were used.

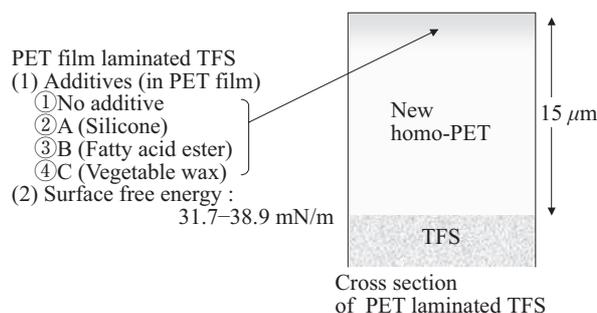


Fig.1 Materials

3.2 Evaluation of Content Release Property

Cup forming was performed with the PET-laminated steel sheet prepared in section 3.1 using a drawing test machine. Next, simulated contents (mixture of eggs, meat, etc.) were packed in the cups and sealed, and retort treatment (121°C, 90 min) was performed. The acceptability of the content release property was judged by the ease of removal and degree of sticking when the contents were removed from the cup. **Table 1** shows the evaluation standard.

3.3 Evaluation of Formability

Formability was evaluated by punching the PET-laminated steel sheets prepared in section 3.1 into circular blanks with a diameter of 100 mm, forming the blanks into cylinders at a drawing ratio of 1.88, filling the cylinders with a 3% NaCl solution, and measuring the current when a DC voltage of 6.2 V was applied.

3.4 Evaluation of Impact Resistance

DuPont impact processing was performed with the PET-laminated steel sheets prepared in section 3.1 using a 1/4R inch (0.64 cm) hemispherical punch, a load of 1 kg, and a drop height of 30cm so as to produce a convex shape on the laminated surface. Impact resistance was evaluated by immersing only the processed part in a 3% NaCl solution and measuring the current at DC 6.2 V.

3.5 Measurement of Surface Free Energy

Surface free energy was derived using the equation proposed by Owen, Young et al⁵⁾. based on measurements of the contact angle between the specimens and 5 liquids with known surface free energies. Measurements of the contact angle were performed by the sessile-drop method by dropping 5 μl droplets in an atmosphere with an air temperature of 20°C and relative humidity of 50±10%.

3.6 X-ray Diffraction Measurements⁶⁾

As an index of the biaxial orientation (BO) of the PET film after lamination, the peak intensity of the (100) crystal plane obtained by X-ray diffraction measurement

Table 1 Evaluation method for content release property

Score	3	2	1	Before taken out
Meat release property	The contents are easily taken out with hardly any content left sticking to the cup.	The contents are rather difficult to taken out with part of the contents left sticking to the cup.	The contents are difficult to take out with much of the contents left sticking to the cup.	① Contents: Mixture of meat, egg ② Retort condition: 121°C, 90min.
Appearance after the contents were taken out				

was used as the BO value. Here, X-ray diffraction measurements were performed by $\text{CuK}\alpha$ at a tube voltage of 40 kV and current of 100 mA, using a RINT2400V device manufactured by Rigaku Corp. In this paper, a value BO/BO_0 , which was obtained by standardizing the BO value after lamination by the BO value before lamination (BO_0), was used as biaxial orientation.

4. Experimental Results

4.1 Results of Study of Content Release Property

The results of an investigation of the effect of surface free energy on the content release property are shown in Fig. 2. A clear relationship can be observed, in which the content release property improves as surface free energy decreases.

The surface free energy of the specimens was adjusted by adding surface-modifying additives to the PET film. Therefore, the effect of each of the surface-modifying additives was investigated. Table 2 shows the surface-modifying additives used here. Additive A

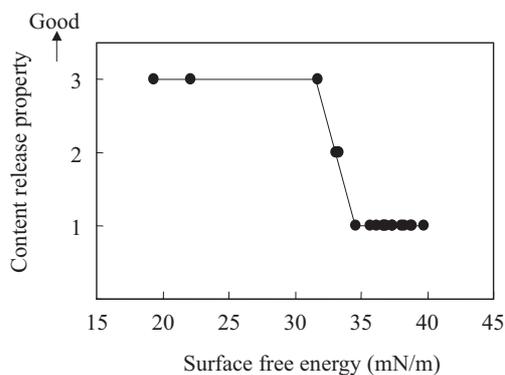


Fig.2 Effect of surface energy on content release property

is silicone and is non-polar. Additive B is a fatty acid ester which has polarity in the carbonyl part, as well as a non-polar part in the hydrocarbon chain. Additive C is a vegetable wax. Like Additive B, it consists mainly of a fatty acid ester, but due to the large carbon number of the hydrocarbon chain, the non-polar part forms the main structure of Additive C.

The effects of these surface-modifying additives are shown in Fig. 3. From these results, it can be understood

Table 2 Variation of additives

	Chemical structure	Model
Additive A : Silicone	$\left[\text{SiR}_2 - \text{O} \right]_n$	 ← Non-polar
Additive B : Fatty acid ester	RCOOR' ($\text{C}_{15} < \text{R}, \text{R}' < \text{C}_{20}$)	 ← Non-polar part (small) ● ← Polar part
Additive C : Vegetable wax	RCOOR' ($\text{C}_{20} < \text{R}, \text{R}'$) and others	 ← Non-polar part (large) ● ← Polar part

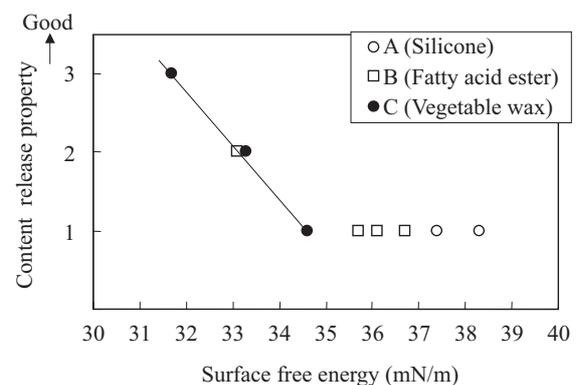


Fig.3 Effect of additives

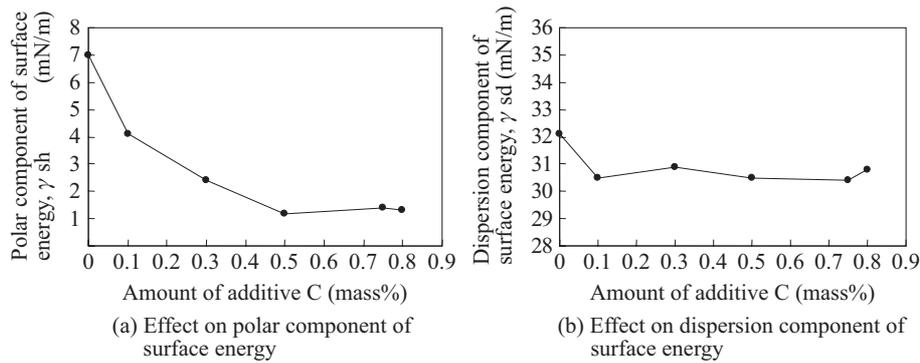


Fig.4 Relation of amount of additive C and components of surface free energy

that addition of Additive C (vegetable wax) reduces surface free energy most effectively and gives a satisfactory content release property. Accordingly, within the scope of research in this report, a surface-modifying additive structure having a polar part and a large non-polar part is effective.

Focusing on Additive C (vegetable wax), the effect of the amount of addition on surface free energy (polar component and dispersive component) was investigated, with the results shown in Fig. 4. From Fig. 4(a), it can be understood that the energy of the polar component decreases as the amount of addition increases. On the other hand, in Fig. 4(b), virtually no change in the energy of the dispersive component can be observed with increasing addition. Accordingly, it was concluded that surface-modifying Additive C (vegetable wax) has an effect which reduces the polar component of surface free energy.

4.2 Results of Study of Formability and Impact Resistance

The results of an investigation of the relationship between BO of PET-laminated steel sheets and their formability and impact resistance are shown in Fig. 5 and Fig. 6, respectively. It can be understood that the formability and impact resistance of the developed steel sheet laminated with the new homo-PET film are excellent in comparison with conventional homo-PET-laminated steel sheets. The formability of the new homo-PET-laminated steel sheet is improved by reducing BO. Where impact resistance is concerned, the current value increases when BO is reduced, indicating deterioration of this property. As seen here, formability and impact resistance show contradictory tendencies. However, it can be understood that a new homo-PET-laminated steel sheet with a good balance of these two properties can be obtained if BO is controlled within the range 0.1–0.6.

4.3 Study of Designability

As the colorant, organic pigments were selected from the viewpoints of safety and tinting strength and added

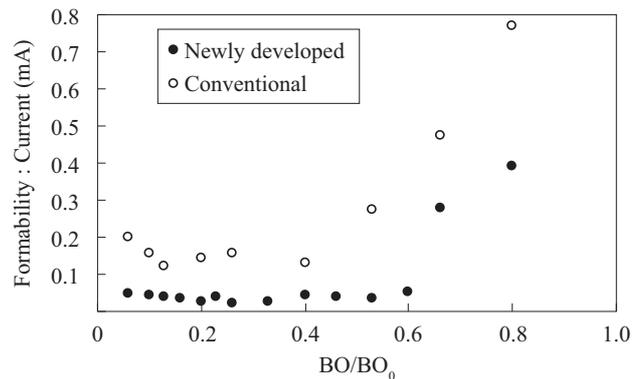


Fig.5 Effect of BO value on formability

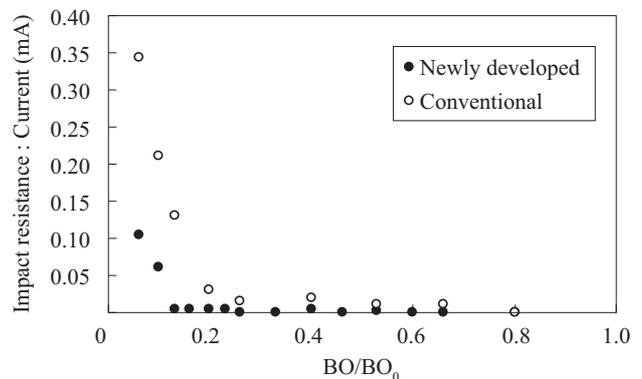


Fig.6 Effect of BO value on impact resistance

to the PET film. Mobility in the PET film was inhibited by adjusting the molecular structure of the pigment, etc. The pigment segregation phenomenon was completely prevented by forming a protective film layer and controlling the crystallographic structure of the PET film.

4.4 Developed Product

The new PET-laminated TFS sheet for food cans developed by JFE Steel is shown in Figs. 7(a) and (b). On the side corresponding to the inside of the can, a PET film with a multi-layer structure is applied. An excellent content release property and formability/impact resistance are realized by adding the designated surface-modifying additives to the top layer and adjusting the biaxial orientation of the film.

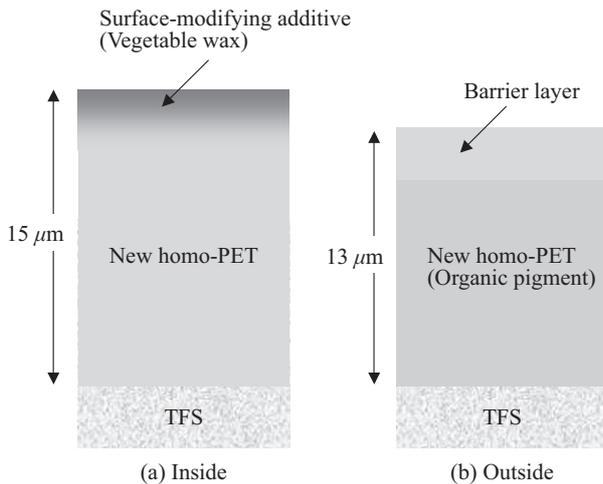


Fig. 7 Cross-section of the new laminated TFS for food cans

A multi-layer PET film is also used on the side corresponding to the outside of the can. Stable, excellent designability is realized by adding the colorant to the bottom layer.

The developed product was produced on a commercial line, and a continuous can-making test was performed on a can-maker's actual production line. The results are shown in **Photo 1**. Two types of cans were produced, a half-pound can and a one-pound can. The sample cans are free of wall breaking, cracks, and wrinkles, demonstrating that the new product has satisfactory properties for can-making. A test of changes over time was also performed after the contents were packed, confirming that satisfactory performance is maintained.

Industrial production of the developed product began in 2001, and large-volume orders have been received, particularly from major can manufacturers in North America. A large increase in orders is expected in the future, and the record of use is steadily increasing on the global scale.

5. Conclusions

A new PET-laminated tin free steel (TFS) sheet for food cans, “UNIVERSAL BRITE[®]” Type F, was devel-

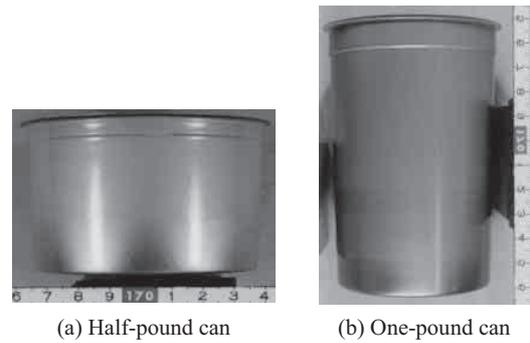


Photo 1 Cans made from the new film laminated TFS

oped. In addition to excellent environment-friendliness, the new product satisfies all performance requirements for food cans, beginning with the content release property, formability, and designability. A summary of the investigation results obtained in the course of product development is presented below.

- (1) The content release property is affected by the surface free energy of the material in contact with the content. Surface free energy can be reduced effectively by adding an appropriate surface-modifying additive (vegetable wax) to the PET film, realizing an excellent content release property.
- (2) Formability and impact resistance were improved by applying a new homo-PET film with a unique amorphous molecular structure and a laminating technology which controls the biaxial orientation of the film within the proper range.
- (3) Segregation of the colorant to the surface of the PET-laminated steel sheet was completely prevented, realizing stable, excellent designability.

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