New Resin-Film Laminated Steel Sheet for 18 *l* Cans and Pail Cans "UNIVERSAL BRITE®" Type E†

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Abstract:

JFE Steel developed and commercialized a resin-film laminated steel sheet called "UNIVERSAL BRITE®" Type E which is applicable to large cans such as 18 l cans and pail cans using a newly-developed 2-layer polypropylene (PP) film. In the main layer, the requirements of flexibility and heat resistance are both satisfied by using block PP, while good adhesion with the steel sheet is secured by an adhesive sublayer consisting of carboxylic acid-modified PP with carboxylic acid-modified polyethylene (PE) added in the optimum ratio. As a result, the new laminated steel sheet is suitable for a wide range of contents, including surfactants. The new sheet also features designability by lacquer painting, as its heat resistance prevents film melting due to the heat of baking when a lacquer coating is applied to the outer side of the can. JFE Steel has also developed a new lineup of polyethylene terephthalate (PET)-laminated steel sheets which respond to a wide variety of customer needs in the field of large cans, including an inside PET-laminated steel sheet for food containers which do not require alkaline resistance and an outside PET-laminated sheet for paint and solvent cans without an inside coating.

1. Introduction

In the field of metal cans, as represented by steel cans, painting has been used to improve corrosion resistance. After painting, the painted cans are repeatedly heated several times to around 150°C–200°C for approximately 10–20 min. For this reason, treatment of volatilized organic solvents, CO_2 emissions, and excessive energy consumption have become important issues from the viewpoints of the global environment and the labor environment.

In recent years, laminated cans coated with a thermoplastic resin film as a substitute for paint have attracted considerable attention, and the changeover from painted cans is progressing rapidly, centering on steel beverage cans and food cans[1,2)]. Because the painting and baking processes can be eliminated, it is possible to reduce releases of organic solvents and CO_2 emissions and decrease energy consumption. Thus, in comparison with conventional painted cans, resin-laminated cans are recognized as an environment-friendly type of can.

Recently, the changeover to laminated cans has also spread to the field of 18 *l* cans and pail cans, as represented by 18 *l* cans (**Photo 1**) and pail cans[3)].

To date, examples of practical application of lami-

Photo 1 An example of 18 *l* can made of "UNIVERSAL BRITE" type E

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nated steel sheets in the 18 *l* cans and pail cans field include a product which is manufactured by the can maker in 1-sheet units by laminating a thick polyethylene (PE) film to electrolytically chromium coated steel (ECCS) in sheet form, and a product made by laminating a thick film of random polypropylene (PP) (PP-PE random copolymer) on ECCS by direct extrusion of the molten resin from a T-die.[3)] In both cases, use of these products is limited to some high grade cans due to the high cost of the resin, and they have not reached the stage of wide popularization as an alternative to painted cans, which are inexpensive and are used in large numbers.

Against this background, JFE Steel was the first in the world to develop and commercialize a new resin film-laminated steel sheet, "UNIVERSAL BRITE®" Type E (ecology), which features a lower total can-making cost than painted cans and is applicable to various contents from acidic to alkaline, aiming at popularization of film-laminated 18 *l* cans and pail cans.

2. Concept of Laminated Film Design

Unlike conventional beverage can and food can applications, when film-laminated steel sheets are applied to 18 *l* cans and pail cans, the material must be suitable for a wide range of can contents. This means that the laminated film must be chemically stable in the presence of a wide range of contents, from acidic to alkaline. In addition, the material must also provide corrosion resistance against surfactants such as detergents, which are typical contents of 18 *l* cans and pail cans.

In many cases, the exterior of the can is lacquer-painted to indicate the contents or impart design features. However, if the heat resistance of the film is inadequate, sticking in the oven due to film melting becomes a problem. Although there has been trend toward lower baking temperatures in recent years as a means of saving energy, the baking temperature is normally 140–150°C, which means that the film must have a melting point of >150°C to ensure stable baking.

For a variety of reasons, high film adhesion is also required. For example, if film adhesion is inadequate, the pressure-resisting strength of the seamed part between the can end and body may be inadequate due to delamination of the film, and underfilm corrosion can easily proceed if the film is damaged by impact.

For laminated cans to replace painted cans, the film cost must be competitive with painting costs.

Polyethylene terephthalate (PET), which is widely used in beverage and food containers, is relatively economical and is stable against neutral-to-acid substances. However, PET is not suitable for general-purpose applications as the film is decomposed by hydrolysis in alkaline environments, limiting its application. Polyolefin resin such as PP and PE can be mentioned as resins which do not contain harmful substances, are inexpensive, and are stable under acidic to alkaline environments. Among these, the melting point of PP is approximately 160°C, while that of PE is about 120°C. That is, PP secures the necessary melting point of >150°C.

On the other hand, because PP is a polymer with poor adhesion, it generally does not adhere strongly to an ECCS substrate. To improve adhesion, a modified PP, in which a polarity group such as carboxylic acid is introduced into the PP molecular chain is used generally. However, because modified PP is more expensive than unmodified resins, use of a modified PP in the full film layer would invite higher costs.

Therefore, as shown in **Fig. 1**, a 2-layer structure was adopted by using a high melting point PP resin in the main layer to secure high heat resistance, and providing an adhesion layer of a modified resin as an sublayer under this. The thickness of the adhesion layer can be minimized within the range where a uniform thickness can be maintained. In practical terms, this means a thin film of 3–5 μm, as uniform film-forming is possible. Adoption of this structure can reduce consumption of expensive modified resin and make it possible to reduce the cost of the resin film to the same level as painting or less. Thus, it is possible to satisfy the property requirements of the film as a whole by imparting separate functions to the respective layers of the 2-layer film and optimizing the design of each. Specifically, the main layer resin must satisfy both heat resistance (melting point >150°C) and corrosion resistance against surfactants, while the adhesion layer resin is required to provide adhesion with the main layer film and substrate ECCS. The following describes the film design of the main layer and adhesion layer.

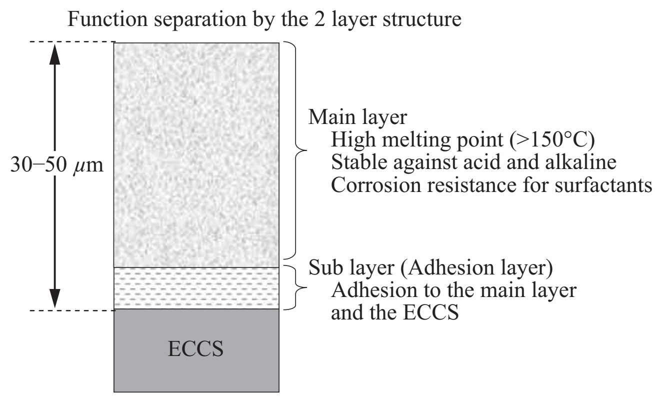


Fig. 1 Concept of the laminating film for 18 *l* cans and pail cans

3. Design of Main Layer to Satisfy Heat Resistance and Surfactant Corrosion Resistance

3.1 Experiment Method

The material used as the substrate steel sheet for laminating was ECCS, which was produced by chrome plating both sides of tin mill black plate (TMBP; Temper degree: T4CA, Thickness: 0.32 mm) using a CrO_3-F^--SO_4^{2-} plating bath, and performing electrolytic chemical treatment using a CrO_3-F^- chemical treatment bath.

The resin film used in lamination was a PP-PE composite-type 2-layer film formed by a non-oriented film-forming process by coextrusion. A mixture of carboxylic acid-modified PP and carboxylic acid-modified PE was used in the adhesion layer. The test materials for the main layer were homopolymer PP (homo-PP), and block PP (PP-PE block copolymer), which was produced by block copolymerization of several percent of PE in PP. For comparison, random PP, which was produced by random copolymerization of several percent of PE in PP, was used in some tests. The thickness of the adhesion layer film was 5 μm, and that of the main layer was 45 μm, for a total film thickness of 50 μm.

The ECCS used as the substrate was heated to 200°C, and the above-mentioned 3 types of PP films were laminated by thermal bonding.

Heat resistance was evaluated, as shown in **Fig. 2**, by placing a glass ring with a diameter of 60 mm and a load of 100 g on the laminated steel sheets, holding the specimen for 15 min in a heating furnace kept at 150°C, and checking for the presence of melting marks after removing the glass ring.

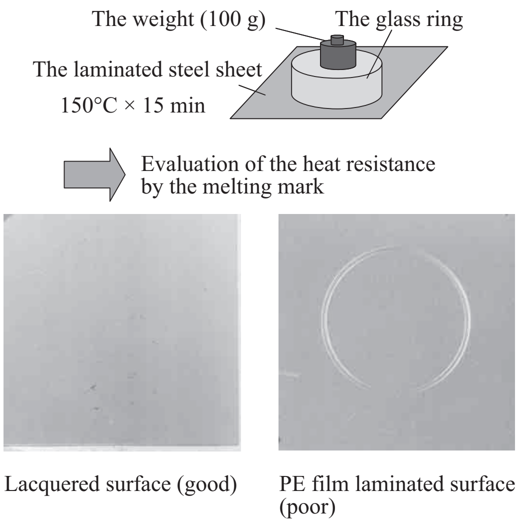


Fig. 2 Example of the evaluation of the heat resistance

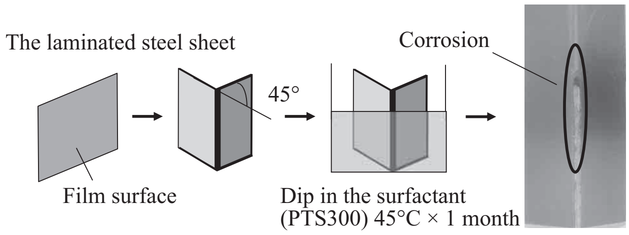


Fig. 3 The evaluation of the corrosion resistance for surfactants

The evaluation method for corrosion resistance for surfactants is shown in **Fig. 3**. The laminated steel sheet was subjected to 45° convex bending (forming simulating the embossed part and cap processing part on the inside of a 18 *l* can). The specimen was immersed in a strongly acidic surfactant (PTS300; manufactured by Yushiro Chemical Industry Co., Ltd.) at 45°C for 1 month, after which it was visually inspected for corrosion and the cross section of the processed part was observed by transmission electron microscope (TEM). In the TEM observation, dye treatment with ruthenium(IV) oxide was performed as considered appropriate to heighten the contrast of the resin.

3.2 Results of Heat Resistance and Corrosion Resistance Evaluation and Discussion

Photo 2 shows the results of a heat resistance test of laminated steel sheets with various types of films. homo-PP has the highest melting point among the PP resins, and no melting marks were observed after heat treatment at 150°C. In contrast, with a main layer of random PP, clear melting marks could be seen on the resin. Because random copolymerization with PE rapidly reduces the melting point of PP, it can be understood that 150°C heat resistance cannot be maintained when copolymerization exceeds only a small several %. Thus, application of random PP in the main layer resin is difficult from the heat resistance. On the other hand, as with homo-PP, no melting marks were observed with block PP, and it can therefore be understood that this material displays excellent heat resistance.

Photo 3 shows the results of a corrosion resistance test for surfactants performed using main layers of

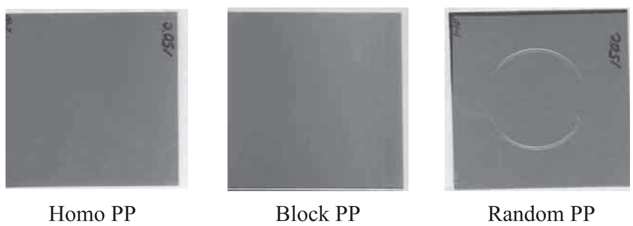
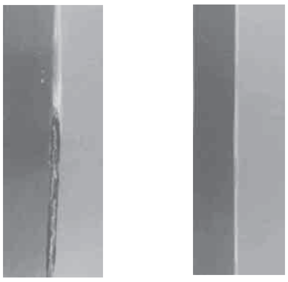


Photo 2 The results of evaluation of the heat resistance



Homo PP Block PP

Photo 3 The results of evaluation of the corrosion resistance for surfactants

homo-PP and block PP, which showed excellent heat resistance. With homo-PP, no corrosion was observed in the flat area, but corrosion could be seen in the convex bent part. In contrast, with block PP, no corrosion was observed in either the flat part or the convex bent part, showing excellent corrosion resistance for surfactants.

In the case of surfactants with strong infiltration, if even tiny cracks exist in the convex bent part, which are subjected to tensile stress, the cracks will grow as the surfactant infiltrates from this part, resulting in corrosion when the cracks reache the steel sheet. Increasing the flexibility of the resin, thereby relieving the tensile stress in the film, is an effective means of preventing the growth of cracks (stress cracks) in this type of processed part. Polypropylene randomly copolymerized with PE is flexible, and thus is less susceptible to stress cracking than homo-PP. However, due to the rapid decrease in the melting point of the copolymerized resin, as mentioned above, it is difficult to satisfy both flexibility and heat resistance requirements. Conversely, if random copolymerization is limited to a very slight amount of PE to keep a melting point of 150°C, it is difficult to obtain any remarkable effect in preventing stress cracking.

In contrast to this, block PP characteristically forms a structure in which PE particles are dispersed in the PP matrix, as shown in **Fig. 4**. Moreover, in this case, ethylene propylene rubber (EPR) forms at the grain boundaries between the PP matrix and the PE particles. When bending or similar forming is performed, the flexible PE particles and surrounding rubber parts relieve the stresses generated by forming, and thus have the effect of preventing cracking. **Photo 4** shows a TEM image of the film cross section at a convex bent part after immersion in PTS300. In the case of homo-PP, a large number of stress cracks can be observed in the resin. In contrast, with block PP, although deformation of the PE particles can be observed, no cracks have formed.

Furthermore, with block PP, the melting point of the resin is substantially controlled by the PP surrounding the PE particles. Therefore, in actuality, no extreme reduction of the melting point can be seen, even with addition of nearly 40% of PE[4]. In other words, due to

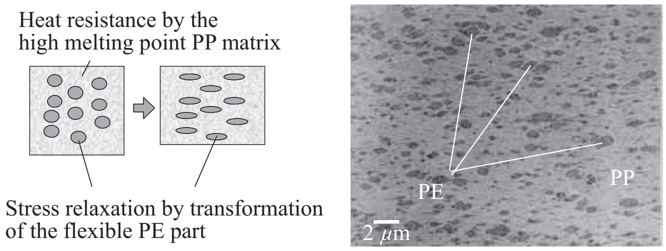
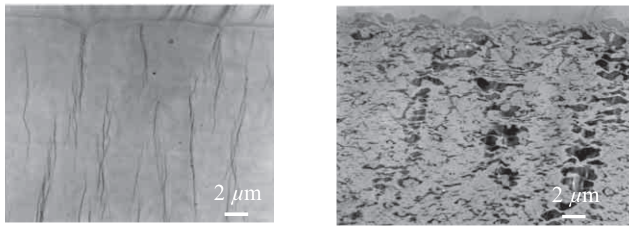


Fig. 4 The schematic diagram and TEM image of the block PP



Homo PP Block PP

Photo 4 The cross sectional TEM images of the bended part of films (After dipping in PTS300, 45°C × 1 month)

the characteristic dispersed structure of PE particles, block PP can satisfy both heat resistance and corrosion resistance for surfactants, and is suitable as the main layer resin for laminated sheets for 18 *l* cans and pail cans.

4. Improvement in Adhesion of Adhesion Layer Resin

4.1 Experimental Method

As the substrate steel sheet for lamination, ECCS (Thickness: 0.32 mm) was used. This material was the same as that used in the study of the main layer resin.

The resin film used in lamination was a non-oriented PP-PE composite-type 2-layer film which was formed by coextrusion. The block PP investigated in Chapter 3 was used in the main layer. The resins used in the adhesion layer were carboxylic acid-modified PP and mixed resins prepared by adding carboxylic acid-modified PE to carboxylic acid-modified PP, with the mixing ratios changed in a stepwise manner. The thicknesses of the adhesion layer and main layer were 5 μm and 45 μm, respectively, for a total thickness of 50 μm.

The ECCS substrate was heated to 200°C, and the above-mentioned films were laminated by thermal bonding.

The following two types of adhesion tests were performed. One was the alkali cross-cut test, in which cross-cuts were made on the laminated steel sheet, and the sheet was immersed for 2 weeks in an alkali solution (20 g/*l* NaOH solution, 38°C), after which the width of film delamination from the cut parts was measured. The second adhesion test was the T-peel test[5], in which laminated steel sheets cut to a width of 5 mm were stacked with the film surfaces together on the inner side, the specimen was pressure bonded at 200°C and 5 kg/cm^2, and delamination strength was measured with a tensile testing machine.

4.2 Results of Adhesion Evaluation and Discussion

Figure 5(a) shows the effect of the carboxylic acid-modified PE ratio in the adhesion layer on the delamination width in the alkali cross-cut test. Because the film has alkaline resistance, in an alkali environment, delamination proceeds due to dissolution of the hydrated chromium oxide in the ECCS surface layer. Thus, this test provides the adhesion strength between the adhesion layer resin and the substrate ECCS. Because the delamination width of the paint film when the same test is performed with painted cans is 1 mm, a result of 1 mm or less was considered satisfactory in this test. With the adhesion layer containing no carboxylic acid-modified PE, the lamination width was 2.3 mm, showing that adhesion with ECCS is inferior to that in painted cans. In contrast, delamination decreases as the carboxylic acid-modified PE ratio in the adhesion layer increases and can be reduced to 1 mm or less. This is estimated to be the result of the increased wettability of the melt resin during lamination due to addition of the low melting point carboxylic acid-modified PE.

Figure 5(b) shows the effect of the carboxylic acid-modified PE ratio in the adhesion layer on film adhesion strength (delamination strength) in the T-peel test. Film adhesion strength decreases as the carboxylic acid-modified PE ratio increases. If film adhesion strength is low, the film will delaminate at seaming parts when the can internal pressure increases, and it will be impossible to obtain adequate pressure-resisting strength. Based on the pressure-resisting strength during actual can-making, the lower limit of film adhesion strength was set at 1.7 kg/5 mm, and the upper limit on the carboxylic acid-modified PE ratio was set accordingly.

Summarizing this discussion, when the carboxylic acid-modified PE ratio is low, delamination occurs at the interface between the adhesion layer and ECCS, but as the ratio increases, this shifts to interlayer detachment between the main layer and the adhesion layer. This shows that interlayer adhesion strength with the main layer decreases as the carboxylic acid-modified PE ratio increases.

Because strong adhesion with both the main layer and the substrate ECCS is required in the resin of the adhesion layer, the carboxylic acid-modified PE ratio in the adhesion layer must be designed in the proper region between a lower limit determined by adhesion with the substrate ECCS and an upper limit determined by adhesion with the main layer. The feature of the adhesion layer in "UNIVERSAL BRITE®" Type E is the balance of melt resin wettability at the interface between the resin film and steel substrate during thermal bonding and interlayer adhesion between the adhesion layer and main layer. This is obtained by blending the optimum amount of low melting point carboxylic acid-modified PE in carboxylic acid-modified PP in the adhesion layer, as described above.

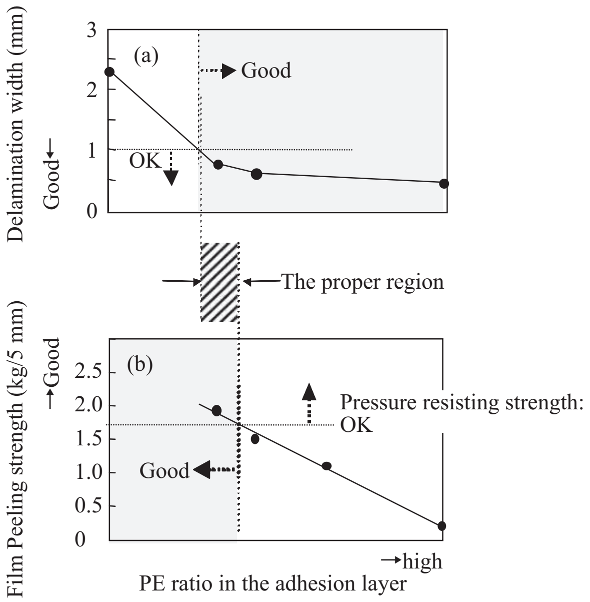


Fig. 5 Influence of the carboxylic acid modified PE ratio in adhesion layer on (a) cross-cut part corrosion resistance and (b) film adhesion strength

5. Corrosion Resistance of "UNIVERSAL BRITE®" Type E

"UNIVERSAL BRITE®" Type E has applicability to a wide range of can contents, from acidic to alkaline, because stress cracks are prevented by the flexible main layer resin and the interfacial adhesion of the adhesion layer has been improved. **Photo 5** shows examples. In a DuPont impact test (1/4*R* punch, 1 kg weight, 15 cm drop height), convex bending equal to or exceeding that in the embossed parts of 18 *l* cans was performed, and specimens were immersed for 1 month at 45°C in an acidic test solution (1.5% citric acid + 1.5% NaCl), neutral test solution (surfactant: Lipon F manufactured by Lion Corp.), and alkaline test solution (20 g/*l* NaOH). Because corrosion resistance of processed parts equal to or better than that of conventional painted cans was confirmed in all regions from acidic to alkaline, laminated steel cans can be expected to replace painted cans with many contents.

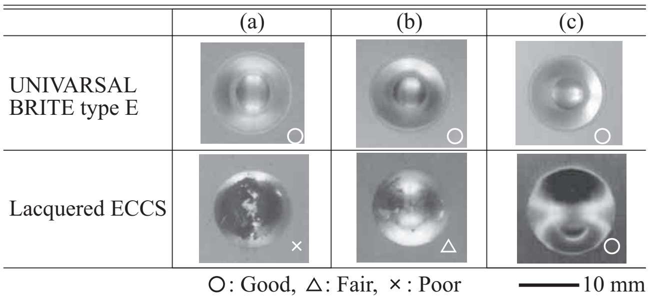


Photo 5 Corrosion resistance of “UNIVERSAL BRITE” type E in (a) 1.5% citric acid + 1.5% NaCl, (b) Neutral surfactant (Lipon F), and (c) 20 g/*l* NaOH at 45°C × 1 month

6. Status of Practical Application and Development of Expanded Range of Applications

The first order for “UNIVERSAL BRITE®” Type E from a large manufacturer of 18 *l* cans was received in May 2002, and sales volume has increased steadily since that time. The 18 *l* cans and pail cans shown in Photo 1 is an example of can-making of welded cans using ECCS for welded cans (JFE BRITE) as the base material, as a steel sheet which enables grinding-free welding. In addition to displaying excellent corrosion resistance for a wide range of contents from acidic to alkaline, including surfactants, this product also realizes high pressure-resisting strength, clearing the standard of the Hazardous Materials Safety Techniques Association, and has earned a high evaluation from customers. This technology was reported on the front page of Metal & Technology of Oct. 15, 2002, and received numerous responses.

Among the applications of 18 *l* cans and pail cans, they are widely used with food products such as sauces, soy sauce, cooking oils, and the like. Because alkaline resistance is not required in these applications, lamination of a PET film is more appropriate in this case, as PET has high corrosion resistance for food ingredients such as organic acids and sulfides and also has a superior flavor property. Using a biaxially-oriented PET film of isophthalic acid copolymerized PET, JFE Steel has developed a practical laminated steel sheet for 18 *l* cans and pail can for food products which satisfies both formability and strength requirements by properly controlling the amount of biaxial orientation of the PET film.

There are also many cases where 18 *l* cans and pail cans are used without an inner coating, for example, in cans for paints and solvents. In such applications, the outside of the can is painted for rust prevention during storage. Responding to customers’ needs for cost reduction in this outside painting, JFE Steel proposed and developed a practical new laminated steel sheet in which a PET film is laminated on the outside of the can. Specialization of performance requirements on rust prevention for the can outer surface made it possible to laminate the PET film under a far higher orientation condition than in conventional PET beverage cans, thereby providing higher resistance to outside surface damage (scratches, etc.) than painted cans. This product has earned an excellent evaluation from customers for its high corrosion resistance, even when subjected to rough handling.

As outlined above, JFE Steel is developing new applications for “UNIVERSAL BRITE®” Type E aiming at application to a wider range of contents and a wider range of applications in the field of 18 *l* cans and pail cans. The company now offers a lineup which can cover a wide range of applications, including general-purpose applications, food product applications, and applications with an uncoated inner side.

7. Conclusions

JFE Steel developed a new resin film-laminated steel sheet for 18 *l* cans and pail cans, “UNIVERSAL BRITE®” Type E. The main layer of the laminated film features an original film design using block PP, which has the following advantages:

(1) Low cost on same level as painted cans
(2) Applicable to a wide range of contents from acidic to alkaline, including surfactants
(3) High heat resistance, enabling lacquer painting of the outside can surface for design purposes

JFE Steel was the first maker in the world to develop a practical new resin film-laminated can material with these features, and is supplying this product to a wide range of users. The company has also added a laminated steel sheet with an inner PET coating for food products and a laminated sheet with an PET outer coating for applications such as paint and solvent containers where no inside coating is used, and is continuing to develop application which respond to a wide range of customer needs in the 18 *l* cans and pail cans field.

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