

Factors Affecting Coating Adhesion of Wax-Added Laminated Steel Sheets

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Abstract:

Wax-added polyethylene terephthalate (PET) films are used in laminated steel sheets for demanding can-forming applications. However, wax addition tends to reduce coating adhesion. This study investigates the effect of wax on coating adhesion using surface free energy analysis. Results show that wax reduces the dipole force component (γ^p) of PET film surface energy, which in turn lowers the work of adhesion between the film and the coating. X-ray photoelectron spectroscopy revealed that this reduction in γ^p is due to a decrease in ester bonds on the PET surface as wax concentration increases. The coating adhesion of laminated steel sheets correlates with the work of adhesion, indicating that wax-induced adhesion loss is attributable to reduced γ^p . These findings suggest that optimizing wax content is essential to balance lubricity and coating adhesion in laminated steel sheets.

1. Introduction

In recent years, products using polyester film-laminated steel sheets have been applied widely in the beverage can and food can sectors^{1,2)}. In comparison with conventional painted materials, laminated steel sheets offer significant advantages, as manufacturing costs can be reduced by omitting the painting and baking processes, organic solvents and other hazardous substances can be eliminated from the manufacturing process, etc.^{2,3)}. The basic properties required in these laminated steel sheets for cans are formability, corrosion resistance and film adhesion with the steel sheet. In addition, when direct printing on the film surface is performed to allow identification of the can contents from outside or to apply design features, adhesion between the laminated steel sheet and the coating used

in printing is also indispensable. On the other hand, when a laminated steel sheet is subjected to demanding forming such as deep drawing, wax is added to the can exterior film to reduce the friction coefficient during forming⁴⁾. Addition of wax generally improves lubricity, contributing to good formability, but coating adhesion tends to decrease. Thus, a product design that provides a balance of lubricity and coating adhesion is required in applications in which deep-drawn laminated steel sheets are to be printed.

The factors that affect coating adhesion include intermolecular forces, primary bonding, mechanical bonding, internal stress, etc. To date, some reports have examined the relationship between these factors and residual stress after can-forming⁵⁾. However, few studies have focused on changes in surface properties due to additives in the film or the changes in intermolecular force accompanying those changes⁶⁾. Therefore, in this research, specimens were prepared by adding varying amounts of wax to a PET film, the differences in the surface free energy of the laminated steel sheets were investigated, and the effect of the intermolecular force on coating adhesion was evaluated. In addition, the factors with large effects on coating adhesion were also studied using the work of adhesion with the coating.

2. Experimental

2.1 Sample Materials

The base laminated steel sheet used in this study was chrome plated steel sheet (tin free steel (TFS)) with a sheet thickness of 0.22 mm. Samples were prepared by thermal fusion of the six types of films shown in **Table 1** to the surface of TFS heated to a temperature higher than the melting point of the film, followed by

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Table 1 Laminated films examined in this study

No.	Polymer	Additive	Amount of additive (wt%)
1	PET	—	—
2	PET	PE WAX	0.05
3	PET	PE WAX	0.10
4	PET	PE WAX	0.20
5	PET	PE WAX	1.00
6	Nylon6	—	—

water cooling and heating for 10 min in a hot air oven at 180°C. In Table 1, No. 1 is a laminated steel sheet in which a biaxially oriented polyethylene terephthalate (PET) film (melting point: 248°C, thickness: 20 μm) copolymerized with isophthalic acid was applied to the substrate TFS sheet by thermal fusion. No. 2 to No. 5 are laminated steel sheets with thermal fusion wax-added PET films in which 0.05, 0.10, 0.20 or 1.00 wt% of added polyethylene (PE; melting point: 125°C) wax was added to a PET film having the same composition as No. 1. As a comparison material, No. 6 is a laminated steel sheet prepared in the same manner but with a film of nylon 6 instead of PET. This material has lower surface free energy than the PET-based laminated steel sheets, as well as different ratios of each component of surface free energy. These test materials were designed to enable a systematic evaluation of changes in surface properties due to the difference in the amount of wax addition, and were used in the analysis of the factors influencing coating adhesion.

2.2 Coating Adhesion Test

Coated specimens were prepared by applying a polyester-melamine-based coating simulating a printing material to laminated steel sheets having films No. 1 to No. 6 using a printability tester (Kumagaya Riki Kogyo Co., Ltd.), followed by baking treatment for 1 min in a hot air drying furnace set to 215°C.

In the evaluation of coating adhesion, a variable normal load friction and wear measurement system (Shinto Scientific Co., Ltd., HEIDON HHS 2000) was used. In the tests, a sapphire probe (tip radius R: 0.6 mm) was placed in contact with the coating surface of the polyester-melamine-coated laminated steel sheet, and the load was changed continuously from 10 g to 500 g under conditions of a sweep rate of 2 mm/s and migration length of 30 mm. The frictional force when peeling of the coating occurred during sweeping was defined as the frictional force for coating peeling (hereinafter, “coating peeling load”), and was quantified as an index of coating adhesion.

Table 2 Surface free energy of liquids

Liquids	Surface free energy (mN/m) ⁷⁾			
	γ_L	γ_L^d	γ_L^p	γ_L^h
Water	72.8	29.1	1.3	42.4
Glycerol	63.4	37.4	0.2	25.8
Formamide	58.2	35.1	1.6	21.5
Ethylene glycol	47.7	30.1	0	17.6
Methylene iodide	50.8	46.8	4.0	0
α -Bromo naphthalene	44.6	44.4	0.2	0

2.3 Measurement of Surface Free Energy and Calculation of Work of Adhesion

Using the six liquids with known surface free energy⁷⁾ (deionized water, glycerol, formamide, ethylene glycol, methylene iodide, α -bromo naphthalene) shown in Table 2, the static contact angles between each liquid and test specimen and coated surface were measured with a contact angle meter (Kyowa Interface Science Co., Ltd., type CA-D). The measurements were performed under an environment at room temperature (20°C) and relative humidity of 50 $\pm$ 10% by the drop method by dropping 2 μL of the droplet. Using the measured values of the contact angle obtained with each liquid and the known values of surface free energy, six equations were constructed from the equation (1) proposed by Kitazaki and Hata, et al.⁷⁾ based on the extended Fowkes theory, and the respective force components of surface free energy were calculated by a method in which error was minimized by linear regression⁸⁾ to obtain the dispersive force component γ^d , dipole force component γ^p and the hydrogen-bonding force component γ^h .

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^d\gamma_L^d} + 2\sqrt{\gamma_s^p\gamma_L^p} + 2\sqrt{\gamma_s^h\gamma_L^h} \dots\dots\dots (1)$$

The work of adhesion W_a between the laminated steel sheet and polyester-melamine coating was calculated by Eq. (2), which combines the Young-Dupré equation and Eq. (1), enabling a quantitative evaluation of the contribution of the intermolecular forces at the interface.

$$W_a = W_a^d + W_a^p + W_a^h = 2\sqrt{\gamma_1^d\gamma_2^d} + 2\sqrt{\gamma_1^p\gamma_2^p} + 2\sqrt{\gamma_1^h\gamma_2^h} \dots\dots\dots (2)$$

2.4 X-Ray Photoelectron Spectroscopy (XPS) Measurement

To evaluate the elemental composition and chemical bonding state of the laminated steel sheet film surface, measurements were performed by X-ray photoelectron spectroscopy (XPS) using an SSX-100 XPS system (SSI; Software Science, Inc.). A monochromatized Al

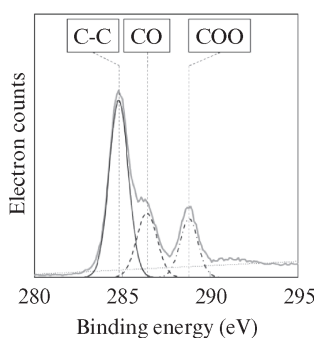


Fig. 1 C1s spectra of X-ray photoelectron spectroscopy of sample1

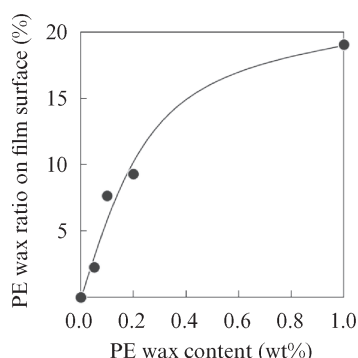


Fig. 2 Relationship between PE wax content and PE wax ratio on film surface

K α beam was used as the X-ray source. The measurement conditions were a measurement region of 600 μ m, accumulation of 6 times and photoelectron take-off angle (TOA) of 35°.

Using the difference between the atomic ratio of O (O_{sa}) obtained from the wide scan spectrum of the laminated steel sheets in which the specified percentages of PE wax were added to the PET film, and the atomic ratio of O (O_p) of PET film No. 1 without wax addition, the ratio of the PE wax on the film surface was calculated by the following Eq. (3).

$$\text{Surface wax ratio (\%)} = (O_p - O_{sa}) / (O_{PET}) \times 100 \dots (3)$$

The bonding state of C atoms was analyzed from the narrow scan spectrum of the C1s region, as shown in **Fig. 1**. Since a narrow scan spectrum can separate the peaks corresponding to C-C (284.8 eV), C-O (286.4 eV) and COO (288.8 eV), the ratio of these bonding states was calculated from the respective peak areas.

3. Results

3.1 Wax Ratio of PET Film Surface

Figure 2 shows the relationship between the amount

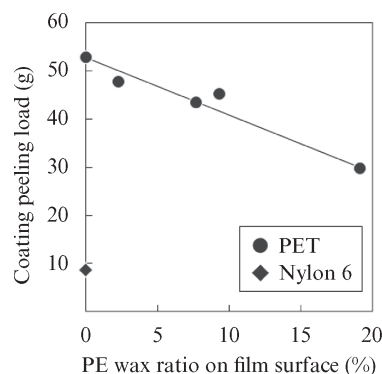


Fig. 3 Relationship between PE wax ratio on film surface and polyester-melamine coating peeling load

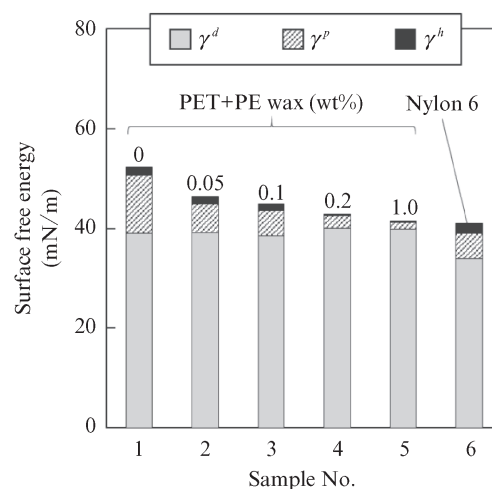
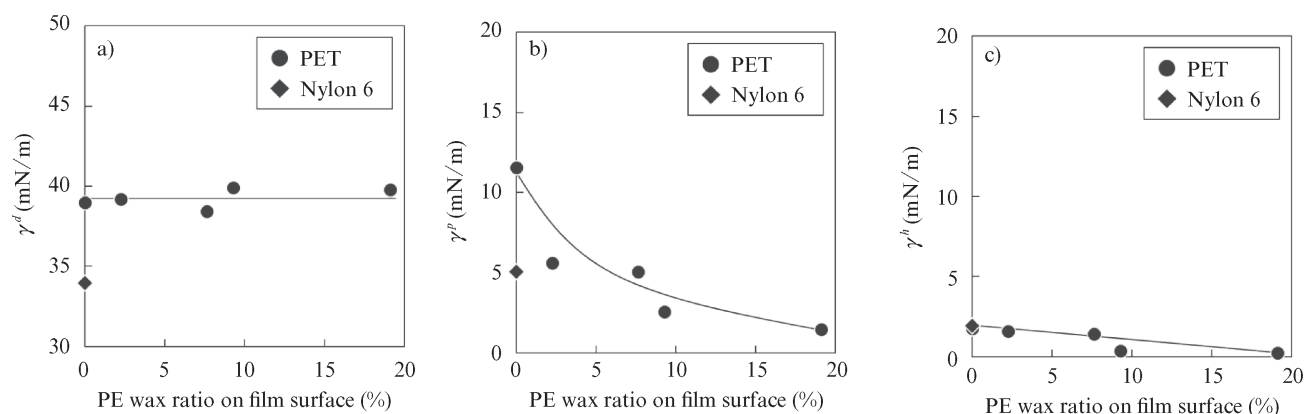


Fig. 4 Surface free energy of laminated steel sheets

of PE wax addition (wax content) and the PE wax ratio on the film surface of the PET-based laminated steel sheets. As wax addition increased, the wax ratio on the film surface also increased. The fact that the wax ratio on the surface is relatively high in comparison with the added wax content in the film suggested that the wax component is concentrated at the film surface.

3.2 Coating Adhesion of Laminated Steel Sheets

Figure 3 shows the relationship between the PE wax ratio on the film surface and the frictional load for coating peeling (coating peeling load) of the laminated steel sheets. In the PET-based laminated steel sheets, the coating peeling load decreased as the wax ratio on the film surface increased. Based on this, wax existing on the film surface is considered to be a factor that inhibits coating adhesion. Specimen No. 6, which was laminated with a nylon 6 film, had a significantly lower coating peeling load than the PET-based laminated steel sheets, indicating that coating adhesion changes not only due to wax addition, but also due to the type of film used on the laminated steel sheet.


 Fig. 5 Relationship between PET wax ratio on film surface and a) γ^d , b) γ^b , c) γ^h

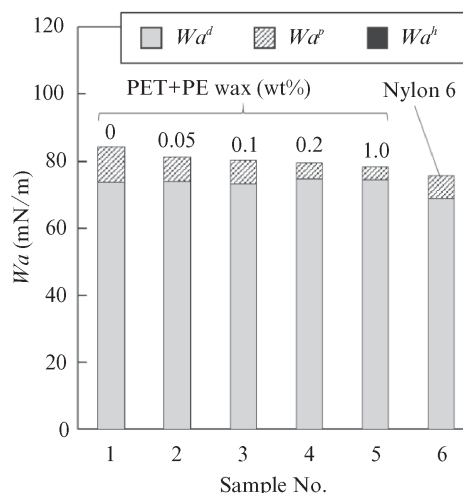
3.3 Surface Free Energy of Laminated Steel Sheets and Work of Adhesion with Coating

The results of calculations of the surface free energy of each test material are shown in **Fig. 4**. The surface free energy of the PET-based laminated steel sheets (No. 1-No. 5) decreased as the amount of PE wax addition increased. The surface free energy of film No. 6, which was laminated with the nylon 6 film, was comparable to that of film No. 5, in which 1.0 wt% of PE wax was added to the PET. However, in comparison with No. 5, the dispersive force component γ^d of surface free energy was smaller, while the dipole force component γ^b and the hydrogen-bonding force component γ^h were larger. **Figure 5** shows the relationship between the PE wax ratio on the PET film surface and the respective components of surface free energy (dispersive force component γ^d , dipole force component γ^b , hydrogen-bonding force component γ^h). The dispersive force component γ^d is constant, independent of the wax ratio. In particular, however, the dipole force component γ^b and hydrogen-bonding force component γ^h decrease as the wax ratio increases. **Table 3** shows the surface free energy of the polyester-melamine coating used in this experiment. The ratio of the hydrogen-bonding force component γ^h of this coating is 0, and the predominant force component is the dispersive force component γ^d .

Figure 6 shows the results of calculations of the work of adhesion W_a (total of the dispersive force component W_a^d , dipole force component W_a^b and hydrogen-bonding force component W_a^h) between the respective specimens and the polyester-melamine coating using Eq. (2). The W_a of the PET film surface decreased as wax addition increased. Among the components that comprise W_a , the contribution of W_a^d is the largest. However, since the dispersive force component γ^d is substantially the same independent of the wax concentration, there are no large differences in W_a^d between the test materials. Furthermore, the poly-

Table 3 Surface free energy of polyester-melamine coating

	Surface free energy (mN/m)			
	γ	γ^d	γ^b	γ^h
Polyester-melamine coating	37.2	34.9	2.3	0


 Fig. 6 Work of adhesion (W_a) between samples and polyester-melamine coating

ester-melamine coating material used here has no hydrogen-bonding force component γ^h ; therefore, W_a^h is also 0 and does not differ depending on the material. These relationships indicated that the only factor that influences W_a is W_a^b , suggesting that the decrease in W_a accompanying increased wax addition is caused by a decrease in the above-mentioned dipole force component γ^b .

On the other hand, the work of adhesion W_a of the nylon 6 film surface is lower than that of the PET film surface with addition of 1.0 wt% of PE wax. This is attributed to the fact that the contribution of W_a^d is the largest of the various components of W_a , and the dispersive force component γ^d of the nylon 6 film surface is smaller than that of the PET film, and it is thought that this difference influenced the frictional

force for coating peeling, that is, the coating peeling load.

4. Discussion

4.1 Influence of Wax Addition on Surface Free Energy

When the surface free energy of the laminated steel sheet films was analyzed separately for the three force components (dispersive force component γ^d , dipole force component γ^p , hydrogen-bonding force component γ^h), a difference in the dispersive force component γ^d of the two film materials, PET and nylon 6, could be seen (Fig. 5a)). In terms of the differences in these types of film, since PET contains an aromatic ring (benzene ring), its electron density is high, and instantaneous induced dipoles between molecules due to the π electron system are strong and tend to act easily. In contrast, nylon 6 has a structure centered on flexible aliphatic hydrocarbon chains. Therefore, its electron concentration is low, and its dispersive force is thought to be relatively weak because it does not have a π electron system⁹⁾. When PET is used as the film base material, its dispersive force component γ^d is constant and is not affected by addition of PE wax. However, a clear decreasing tendency in the dipole force component γ^p and hydrogen-bonding force component γ^h with increases in the wax ratio on the film surface was confirmed (Fig. 5b), c)). These results show that wax addition reduces polar interaction, contributing to a decrease in surface free energy. Therefore, the following discussion considers how the wax that concentrates at the PET film surface influences the dipole force component γ^p and the hydrogen-bonding force component γ^h .

The dipole force component γ^p originates from the electrostatic attraction between dipole moments (interaction between pairs of dipole moments) and induction force (interaction between a dipole moment and an organic dipole moment), and depends on the molecular structure. For this reason, it is necessary to consider the magnitude of the dipole moments of the molecules that comprise the surface. In this study, we conjectured that the addition of PE wax would cause the aliphatic hydrocarbon component^{10,11)}, which does not have a dipole moment, to concentrate at the surface, while the ester bond component contained in PET, which has a high dipole moment, would decrease. Focusing on the PET-based materials, here, the ratio of C assigned to ester bonds on the film surface was calculated by separating the peaks in the XPS measurements. **Figure 7** shows the relationship between the C ratio originating from ester bonds and the dipole force component γ^p . It

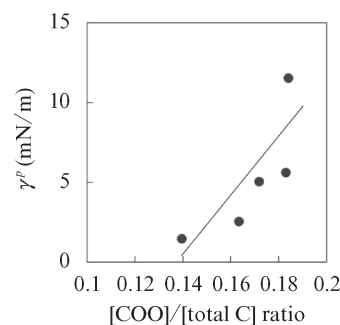


Fig. 7 Relationship between [COO]/[total C] ratio on PET based film surface and γ^p

was found that the ester bonds on the film surface decrease as wax addition increases, and the dipole force component γ^p also decreases accompanying this decrease in the ester bond ratio. It is known that the benzene ring component of PET and the aliphatic hydrocarbon component of PE wax do not have dipole moments, but the C = O bonds of the ester bonds in PET have dipole moments^{10,11)}. Based on this, it is considered that the decrease in the ester bonds at the film surface due to wax addition causes a decrease in the dipole force component γ^p .

Next, although it is thought that hydrogen bonding includes the effects of interorbital interactions and electrostatic attraction¹²⁾, electrostatic attraction is included in the dipole force component γ^p . This means that the hydrogen-bonding force component γ^h is an intermolecular force, which is caused by delocalization of electrons from occupied orbitals to empty orbitals through interorbital interaction. The factors that contribute to interactions that cause delocalization of electrons from occupied to empty orbitals are considered to be oxygen (O) atoms on the ester bonds that exist in PET, together with the terminal carboxyl group and hydroxyl group of PET as a hydrogen donors. The O atoms contained in these functional groups have non-bonding lone electron pairs (occupied orbitals), and affect the hydrogen-bonding force component γ^h by forming interorbital interactions with the empty orbitals of some hydrogen donors of other molecules. Here, **Fig. 8** shows the relationship between the O atomic ratio on the PET-based film surface and the hydrogen-bonding force component γ^h as determined by XPS measurement. As wax addition increases, it was found that the O atomic ratio tends to be lower, and γ^h shows a tendency to decrease as the O atom ratio decreases. The terminal carboxyl group and hydroxyl group in PET are limited to the molecule ends, and the number that exist is extremely small. Therefore, it is estimated that the decrease in γ^h is mainly influenced by a decrease in oxygen atoms in ester bonds, which exist in large numbers as repeating structural units of

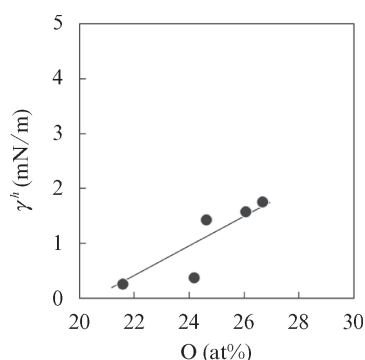


Fig. 8 Relationship between O atom ratio on PET based film surface and γ^h

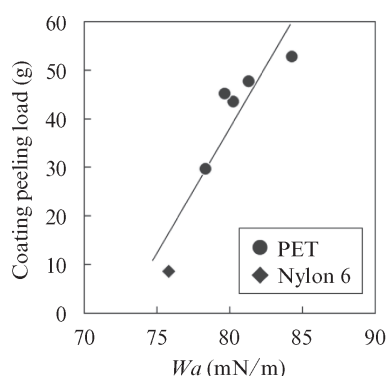


Fig. 9 Relationship between W_a and polyester-melamine coating peeling load

PET. Based on this, it is thought that increasing wax addition decreases the number of ester bonds that exist on the film surface, and accompanying this, the hydrogen-bonding force component γ^h also decreases.

Based on this discussion, the decreases in the dipole force component γ^d and the hydrogen-bonding force component γ^h are considered to occur due to a decrease in the number of ester bonds exposed at the laminate surface accompanying increased wax concentration.

4.2 Relationship between Coating Adhesion and Work of Adhesion

Based on the results presented in Fig. 3 and Fig. 6, in PET-based laminated steel sheets, coating adhesion and the work of adhesion W_a decreased accompanying increases in the wax ratio on the film surface. W_a is the quantity of work necessary to peel off an adhering surface, and is determined by intermolecular force. The relationship between the coating peeling load for the polyester-melamine coating and W_a is arranged in Fig. 9. The fact that the coating peeling load also increased as W_a increased indicates that coating adhesion increases as the magnitude of the intermolecular force between the PET film surface and the coating becomes larger. At the PET film surface, the number of

ester bonds decreases due to wax addition, and the dipole force component γ^d and the hydrogen-bonding force component γ^h change, but since the polyester-melamine coating used in this study does not have a hydrogen-bonding force component γ^h , in this study, in which wax was added to a PET-based film, it can be concluded that the dipole force component γ^d contributed to the work of adhesion W_a , and thus was a factor that affected polyester-melamine coating adhesion.

5. Conclusion

In this research, the factors that decrease coating adhesion in laminated steel sheets with a wax-added PET film were analyzed in terms of surface free energy and work of adhesion. The following knowledge was obtained.

- 1) As wax addition increased, the wax ratio of the film surface also increased, resulting in decreases in the dipole force component γ^d and the hydrogen-bonding force component γ^h of surface free energy. On the other hand, the dispersive force component γ^d was constant, independent of the amount of wax addition. These results show that the decrease in polar interaction due to wax addition contributes to reducing surface free energy.
- 2) The work of adhesion W_a between the laminated steel sheet and the coating decreased as wax addition increased. In particular, the decrease in W_a was predominantly due to the decrease in the dipole force component W_a^d caused by the decrease in the dipole force component γ^d .
- 3) Coating adhesion displayed a tendency to increase as the work of adhesion W_a increased. Therefore, it was suggested that coating adhesion increases as the intermolecular force at the interface between the laminated steel sheet and the coating increases.
- 4) The decrease in coating adhesion associated with addition of wax to PET films is considered to be due to a decrease in intermolecular force caused by a decrease in the dipole force component γ^d with an increased wax ratio at the film surface.

Summarizing these results, this study showed that controlling surface free energy by optimizing the amount of wax addition is a useful guideline for product design for achieving a balance of lubricity and coating adhesion.

References

- 1) Imazu, K.; Sato, K. Development of the Stretch Draw Can made from a Polyester Film Laminated Steel. Shikizai Kyokaishi, vol. 23, no. 10, 1995, p. 622–628.
- 2) Yamanaka, Y.; Kitagawa, J.; Nakamaru, H. Effect of the Surface Free Energy of the Film Laminated Steel Sheet on Content Release Properties. Journal of the Surface Finishing Society of

- Japan. vol. 64, no. 10, 2013, p. 560–564.
- 3) Miyazawa, T.; Imazu, K. A New Development for Can Coating -Laminate-. Journal of the Surface Finishing Society of Japan. vol. 47, no. 8, 1996, p. 677–681.
- 4) Kawai, Y.; Kitagawa, J.; Yoshida, Y.; Kojima, K. Change of surface properties with wax concentration for film surface of laminated steel. Materials and Processes. vol. 31, no. 2, 2018, p. 860.
- 5) Yoshimura, K.; Taya, S. Ink-Adhesion for Two-piece can (TULC) by Non-oriented Polyester Film Laminated Steel Sheet. Toyo Kohan. vol. 37, 2013, p. 1–8.
- 6) Hata, T. Interfacial chemistry of adhesion. Journal of Industrial Chemistry. vol. 73, no. 1, 1970, p. 10–15.
- 7) Kitazaki, Y.; Hata, T. Extension of the Fowkes equation and evaluation of surface tension of polymer solids. Journal of the Adhesion Society of Japan. vol. 8, 1972, p. 131–141.
- 8) Shimoyama, K.; Noshio, S.; Nakamori, H. Method for measuring surface free energy of solids and measuring apparatus therefor. Japanese Patent. JP4012891, 2007.
- 9) Cao, Y.; Wong, M. W. Roles of electrostatic interaction and dispersion in CH...CH, CH... π , and π ... π ethylene dimers. Journal of Molecular Modeling. vol. 20, 2014, p. 2185–2196.
- 10) Israelachvili, J. N. Intermolecular and Surface Forces, 3rd ed. Academic Press. 2011, 704 p.
- 11) Mark, H.; Tobolsky, A. V. Physical Chemistry of High Polymeric Systems, 2nd ed.. Interscience Publishers. 1950, 506 p.
- 12) Iwaoka, M. Contact angle, wettability and adhesion. Gendai Kagaku, Tokyo Kagaku Dojin, Tokyo. 1996, 80 p.