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# Development of Prepainted Steel Sheet with Excellent Formability, Stain Resistance, and Hardness

Hiroshi Kanai*1 Joji Oka*2
Masaya Tsutsumi*3

**Abstract:**

*Paint films prepared by changing the type of polyester resin, melamine-formaldehyde resin, and curing catalyst were examined for the surface structure by X-ray photoelectron spectroscopy. When a polyester resin of low hydroxyl value was combined with an amine-blocked, strongly acidic catalyst and a melamine-formaldehyde resin with the rate of self-condensation reaction being low in the absence of catalyst and high in the presence of strong acid, a melamine-formaldehyde-enriched layer was formed on the paint film surface. This mechanism was studied according to catalytic activity near the paint film surface and the self-condensation of the melamine-formaldehyde resin. It was found that there is a positive correlation between the stain resistance of the paint film and the melamine-formaldehyde resin concentration in the paint film surface, and that the melamine-formaldehyde resin-enriched layer on the paint film surface provides good formability. A new type of prepainted steel sheet with excellent formability, stain resistance, and hardness was developed on the basis of these findings.*

## 1. Introduction

Previously, steel sheets for household electric appliances were formed, assembled, and painted in that order. Recently, however, prepainted steel sheets have come to be used in many applications. Prepainted steel sheets allow household electric appliance manufacturers to eliminate the painting process and thereby solve the problems of worker health and air pollution from solvent discharge. Elimination of the painting process also offers such other advantages as improved productivity, and increased space utilization rate, resulting in cost reduction.

Prepainted steel sheet is destined for press forming and must be highly formable. It will be disastrous if the paint film of worked parts crack or peel and mar the appearance of the product. The paint film must be flexible and strong enough to preclude these defects. Besides formability, prepainted steel sheets must also have surface hardness and stain resistance comparable to steel sheets painted at users' plants. The paint film must be designed to satisfy these two requirements. A paint system in which a polyester resin with a high molecular weight and low functionality is cross-linked by a melamine-formaldehyde resin is generally used now to ensure high formability.

As shown in **Fig. 1**, however, it is difficult to improve hardness and stain resistance while maintaining high formability. The

*1 Technical Development Bureau
*2 Technical Development Bureau (presently Nippon Steel Metal Products Co., Ltd.)
*3 Flat Product Group

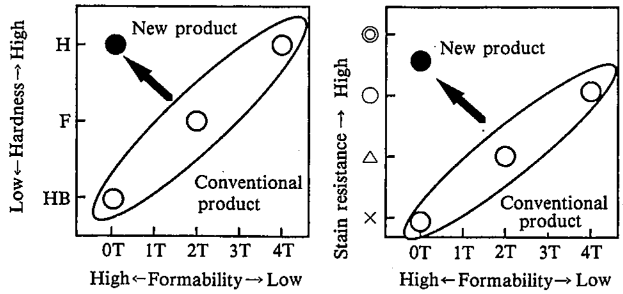


**Fig. 1** Relationship between formability and hardness and between formability and stain resistance: Conventional levels and development goals

conventional paint systems have limitations on their usage: Where there is a strong formability requirement to meet, hardness and stain resistance are sacrificed. Where there are strong hardness and stain resistance requirements to satisfy, formability is sacrificed. Various studies have been made on this issue mainly on the part of paint manufacturers, but paint systems are still poor in the functionality balance, and this is one factor in restricting the application of prepainted steel sheets.

Under these circumstances, the surface structure of polyester resin/melamine-formaldehyde resin paint films was analyzed by X-ray photoelectron spectroscopy (XPS) to determine the relationship between the stain resistance and surface structure of the paint film. Technology was established for controlling the orientation of melamine-formaldehyde resin in the paint film[1,2]. Findings obtained in the course led to the development of a new prepainted steel sheet with excellent formability, hardness, and stain resistance.

## 2. Experimental Methods

### 2.1 Materials

2.1.1 Paint formulations

The polyester resins used as experimental materials are listed in **Table 1**. Three types of polyester resins, designated A, B, and C, were synthesized by changing the hydroxyl value. These polyester resins are practically the same in monomer composition and glass transition temperature, but the constraints of resin synthesis decreases the molecular weight as the hydroxyl value increases. No nitrogen atoms are contained in the polyester resins A to C.

Three types of melamine-formaldehyde resins with different rates of reaction, namely, highly methylated melamine-formaldehyde resin (abbreviated to the methylated type 1), high imino group melamine-formaldehyde resin (abbreviated to the imino type), and partially methylated melamine-formaldehyde resin (abbreviated to the partially methylated type), were selected as the melamine-formaldehyde resins, as listed in **Table 2**. Another highly methylated melamine-formaldehyde resin with a different degree of polymerization (abbreviated to the methylated type 2) was also studied. The relative rate of self-condensation reaction in the absence of catalyst is included for the four types of melamine-formaldehyde resins. The methylated types are known to have a high rate of self-condensation reaction in the presence of a highly acidic catalyst[3,4]. The abbreviations in **Table 2** are used in the figures that follow.

**Table 1** Polyester resins used in experimental study

| Symbol | Type | Hydroxyl value | Glass transition temperature (°C) | Number averaged molecular weight | Weight averaged molecular weight |
|---|---|---|---|---|---|
| A | Linear | 8 | 18 | 19,000 | 59,000 |
| B | Branched | 25 | 22 | 15,000 | 60,000 |
| C | Branched | 40 | 20 | 4,000 | 29,000 |

Commercial rutile titanium dioxide (Ishihara Sangyo CR95) was used as the pigment and was dispersed and mixed to a pigment weight concentration (PWC) of 50% in a paint shaker. Dodecylbenzenesulfonic acid and dodecylbenzenesulfonic acid neutralized and blocked by a volatile amine compound were used as curing catalysts (see **Table 3**). A 1/1 weight ratio mixture of cyclohexanone and Solvesso 150™ was used as thinner whenever necessary.

2.1.2 Preparation of prepainted steel sheet

Electrogalvanized steel sheet, measuring 0.6 mm in thickness, having a zinc coating weight of 20 g/m$^2$ per side, and chromate treated, was coated with a commercial heavy-forming primer of the high-molecular weight polyester resin type and baked to a dry film thickness of 5 $\mu$m. The primed sheet was then coated with the paint formulated as described in 2.1.1 and baked to a dry film thickness of 18 $\mu$m. The baking temperature was set at a maximum sheet temperature of 230°C unless otherwise specified.

### 2.2 Analysis of paint film structure by XPS

The XPS spectra of the paint film surface of the prepainted steel sheet described in 2.1.2 were measured using a Shimadzu ESCA 850 and the Mg K$\alpha$ line as the X-ray source at 7 kV and 30 mA. The XPS spectrum positions were corrected by the peak position of gold. The C1s spectrum was waveform separated by computer into the four peaks of 285 eV CH, 286.5 eV CO, 287.2 eV CN, and 289 eV COO. The ratio of the CN spectrum area obtained by the waveform separation to the total C1s spectrum area was calculated. This ratio is defined as the melamine ring carbon concentration because the CN spectrum is derived from the melamine-formaldehyde resin. The relative number ratios of the carbon, oxygen, and nitrogen atoms were obtained from the peak area ratios of the C1s, O1s, and N1s spectra, respectively.

### 2.3 Evaluation of practical properties of prepainted steel sheet

The stain resistance, pencil hardness, and T-bend ability of

**Table 2** Melamine-formaldehyde resins used in experimental study

| Abbreviation | Type | Degree of polymerization | Rate of self-condensation reaction (in absence of catalyst) |
|---|---|---|---|
| Methylated type 1 | Highly methylated melamine-formaldehyde resin | 1.75 | Low |
| Methylated type 2 | Highly methylated melamine-formaldehyde resin | 1.3 | Low |
| Imino type | High imino group melamine-formaldehyde resin | 2.3 | High |
| Partially methylated type | Partially methylated melamine-formaldehyde resin | 2.6 | High |

**Table 3** Curing catalysts used in experimental study

| Abbreviation | Type |
|---|---|
| Non-neutralized | Dodecylbenzenesulfonic acid (45 wt% isopropanol solution) |
| Neutralized | Non-neutralized dodecylbenzenesulfonic acid neutralized by equivalent addition of volatile amine |

the prepainted steel sheet were evaluated.

Stain resistance: A black oil-based marking ink was drawn on the paint film of the specimen. After the specimen was left to stand at 20°C indoor, it was wiped with ethanol and visually examined to determine the degree to which the line remained. The stain resistance of the paint film was evaluated good when the marking ink did not remain at all and poor when the marking ink did not disappear at all.

T-bend ability: The specimen was thickness bend at 20°C and examined as to the paint film on the bend with a 20 × magnifying glass. The T-bend ability of the specimen was evaluated by the maximum number of thicknesses to which the specimen could be bent without cracking in the paint film.

## 3. Experimental Results and Discussion

### 3.1 XPS analysis of surface structure of paint film

**Fig. 2** shows typical XPS wide-scan spectra of the paint film surface. At the XPS measuring depth, titanium in the titanium dioxide contained in the paint is not observed, and oxygen, nitrogen and carbon, which are derived from the resin, are observed. It is evident that only a resin layer constitutes the outermost surface of the paint film without any pigment component being brought to the surface. When about 3 μm of the paint film is removed, the spectrum reveals a peak attributable to the titanium dioxide. The analysis is continued with attention focused on the elements carbon, oxygen, and nitrogen contained in the resins used.

The nitrogen concentration (N1s %) in the paint film surface was determined by XPS when polyester resins A to C were combined with different melamine-formaldehyde resins and curing catalysts. The results are shown in **Fig. 3**. The polyester and melamine-formaldehyde resins were formulated to a solids content weight ratio of 7/3, and the curing catalyst was added by 1.5% of the resin solids content (no amine contained). The nitrogen concentration in the paint film surface is high only when the polyester resin A or B, the methylated type 1 and 2 melamine-formaldehyde resins, and the amine-blocked curing catalyst are used. When the melamine-formaldehyde resin of the methylated type 1 is used, the nitrogen concentration is not appreciably high if the curing catalyst is not blocked by amine or if the melamine-formaldehyde resin of the partially methylated type or imino type is used.

When the polyester resin C of high hydroxyl value is used, the nitrogen concentration in the paint film surface is not high even if the melamine-formaldehyde resin of the methylated type 1 and the amine-blocked curing catalyst are used in combination. The nitrogen concentration in the paint film surface increases as the hydroxyl value of the polyester resin decreases. **Fig. 4** shows

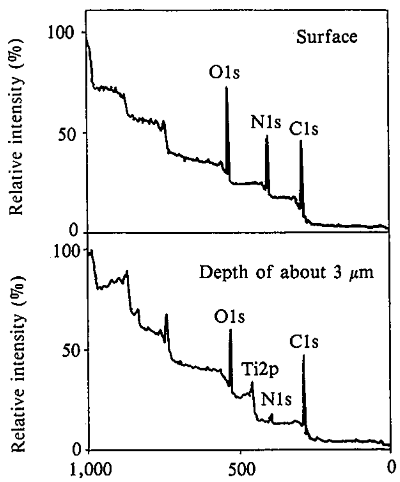


**Fig. 2** Typical XPS spectra of paint film
Top: Spectrum of paint film at surface. Bottom: Spectrum of paint film at depth of about 3 μm.

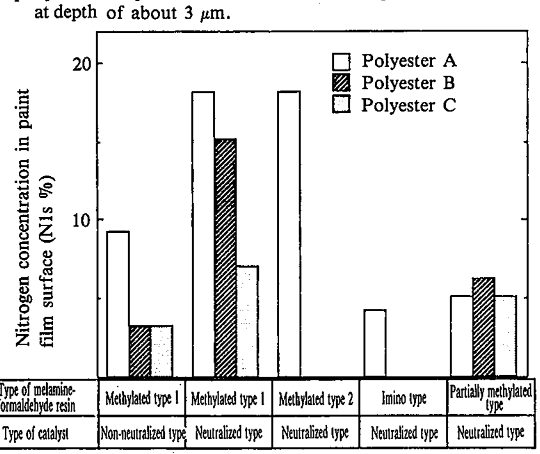


**Fig. 3** Effects of polyester resin type in combination with melamine-formaldehyde resin type and catalyst type on nitrogen concentration (N1s %) in paint film surface
Polyester/melamine-formaldehyde resin = 7/3 (solids weight ratio), Catalyst content 1.5%

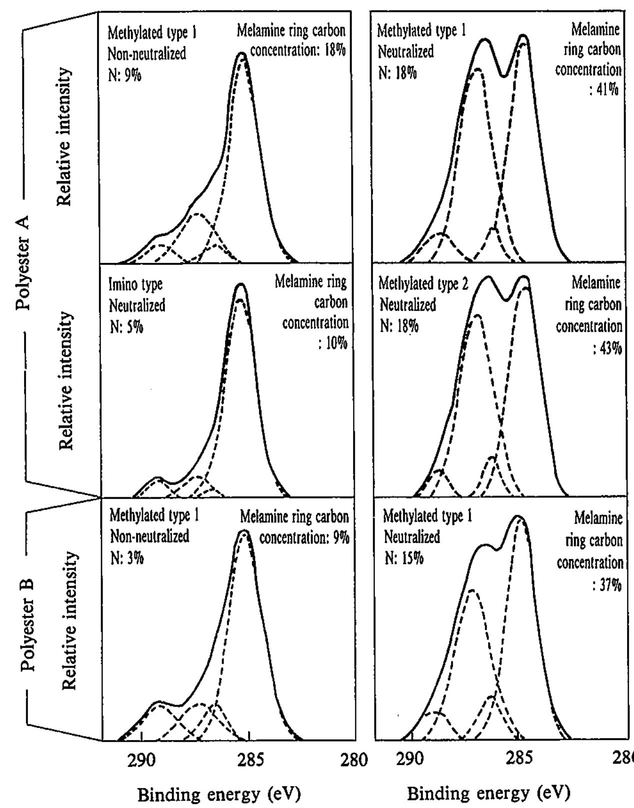


**Fig. 4** C1s spectrum of paint film surface
Polyester/melamine-formaldehyde resin = 7/3 (solids weight ratio). Catalyst 1.5%. Also shown are type of melamine-formaldehyde resin, type of catalyst, nitrogen concentration determined by XPS, and area ratio of CN spectrum to C1s spectrum

the C1s spectra of the XPS survey and the relative atom number ratios of carbon, nitrogen and oxygen for some of the paint films shown in **Fig. 3**. The types of the melamine-formaldehyde resin and curing catalyst used are given at the left shoulder of each spectrum. The area ratio of the CN spectrum to the C1s spectrum after waveform separation is given at the right shoulder of each spectrum. The C1s spectrum group of low nitrogen concentration is arranged on the left-hand side, and the C1s spectrum group of high nitrogen concentration is arranged on the right-hand side.

Characteristically, the peak shape of the C1s spectrum widely varies depending on the magnitude of nitrogen concentration in the paint film surface. A large peak is recognized near 288 eV when the paint film is high in the nitrogen concentration, but this peak is virtually absent when the nitrogen concentration is low. Nitrogen atoms are not contained in the polyester resins but are in the melamine-formaldehyde resins. It is thus presumed that the melamine-formaldehyde resin concentration in the paint film surface is high when a polyester resin of low hydroxyl value is combined with a melamine-formaldehyde resin of the methylated type and the amine-blocked curing catalyst. This thinking is verified by the results of C1s spectrum waveform separation. As shown in **Fig. 4**, the C1s peak of the XPS survey is separated into four waveforms for CH (285 eV), CO (286.5 eV), melamine ring (287.2 eV), and COO (289 eV). When the paint film is high in the nitrogen concentration, the area of the CN peak derived from the melamine-formaldehyde ring is large.

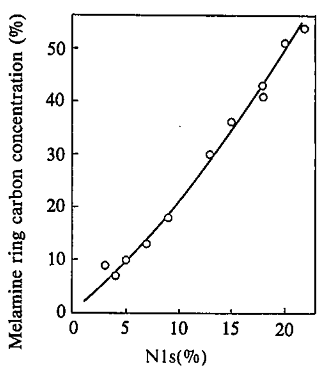


**Fig. 5** Correlation between N1s (%) and melamine ring carbon concentration determined by waveform separation of C1s spectrum

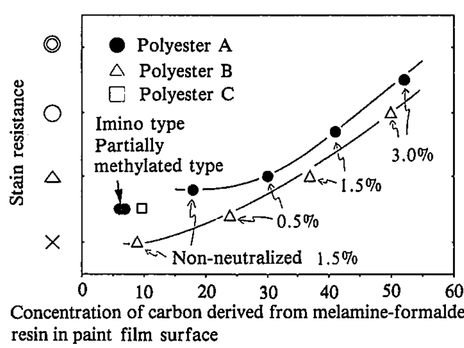


**Fig. 6** Relationship between concentration of carbon derived from melamine-formaldehyde resin in paint film surface and stain resistance of paint film

Polyester/melamine-formaldehyde resin = 7/3 (solids weight ratio). Unless otherwise specified, melamine-formaldehyde resin is of methylated type 1, and catalyst is neutralized and 1.5% in content.

**Fig. 5** shows the relationship between the nitrogen concentration (N1s %) obtained from the peak area and the melamine ring carbon concentration (area ratio of the CN spectrum to the C1s spectrum) obtained from the waveform separation of the C1s spectrum. The good correlation between the two concentrations attests to the validity of waveform separation.

The polyester resins A and B and the melamine-formaldehyde resins were formulated to a polyester/melamine-formaldehyde resin ratio (solids weight ratio) of 7/3, and the catalyst content of the paint was changed. **Fig. 6** shows the relationship between the melamine ring carbon concentration in the paint film surface and the stain resistance of the paint film. Unless otherwise specified, the melamine-formaldehyde resin of the methylated type 1 and the amine-blocked curing catalyst are used. The catalyst content is 1.5%, unless otherwise specified. Increasing the catalyst content increases the melamine ring carbon concentration, which in turn improves the stain resistance of the paint film. When the non-amine-blocked curing catalyst is used or when the melamine-formaldehyde resin is of the imino or partially methylated type, the paint film is low in stain resistance and it is low in the melamine ring carbon concentration.

The melamine ring carbon concentration being equal, the degree of stain resistance varies with the type of polyester resin used. This is reported also by Ikishima et al. for the combination of polyester and butylated melamine-formaldehyde resins[5]. Here, better stain resistance was obtained when the polyester resin A was used. When the polyester resin C of high hydroxyl value is used, the melamine-formaldehyde resin-derived carbon concentration is low, and the stain resistance is poor.

The polyester resins A and B and melamine-formaldehyde resin were formulated to a polyester/melamine-formaldehyde resin ratio (solids weight ratio) of 7/3, and the catalyst content of the paint was changed. The relationship between the melamine ring carbon concentration in the paint film surface and the formability of the paint film is as shown in **Fig. 7**. Unless otherwise specified, the melamine-formaldehyde resin of the methylated type 1 and the amine-blocked catalyst are used. Generally, melamine-formaldehyde resins are harder than polyester resins, so that the paint film tends to decrease in formability when it is high in the melamine-formaldehyde resin content. When the melamine-formaldehyde resin of the methylated type 1 and the amine-blocked catalyst are used, formability can be maintained

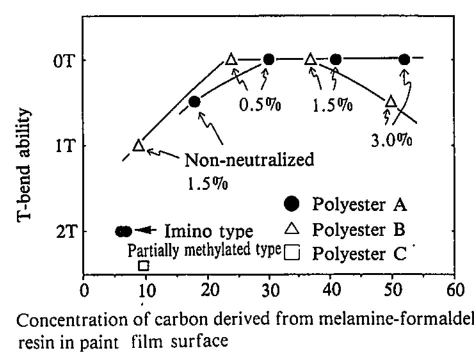


**Fig. 7** Relationship between concentration of carbon derived from melamine-formaldehyde resin in paint film surface and T-bend ability of paint film

Polyester/melamine-formaldehyde resin = 7/3 (solids weight ratio). Unless otherwise specified, melamine-formaldehyde resin is of methylated type 1, and catalyst is neutralized and 1.5% in content.

at 0T despite the high melamine ring carbon concentration in the paint film surface. On the other hand, when the amine-blocked catalyst is not used or when the melamine-formaldehyde resin of the imino type or partially methylated type is used, the melamine ring carbon concentration is low, but the formability level is not high. When the polyester resin B is used, formability drops if the catalyst content exceeds 1.5%. When the polyester resin C of high hydroxyl value is used, formability is poor.

**3.2 Mechanism of melamine-formaldehyde resin enrichment**

As discussed above, the melamine-formaldehyde resin concentration increases in the paint film surface when a polyester resin of a low hydroxyl value is formulated with melamine-formaldehyde resin of the methylated type 1 or 2 and the amine-blocked catalyst. In other words, the melamine-formaldehyde resin tends to be enriched. The mechanism of this melamine-formaldehyde resin enrichment is discussed here.

The equivalent weight ratio of the hydroxyl group of polyester resin to the functional group of melamine-formaldehyde resin is 1/100 or less when a polyester resin with a hydroxyl value of about 8 is formulated with a melamine-formaldehyde resin to a solids weight ratio of 7/3. The equivalent weight ratio is 1/20 or less when the polyester resin has a hydroxyl value of 25. There is only a low probability of the hydroxyl group of polyester resin reacting with the functional group of melamine-formaldehyde resin. The curing reaction is mainly accounted for by the self-condensation reaction of the melamine-formaldehyde resin. Considering this fact as well as the fact that the rate of self-condensation reaction of melamine-formaldehyde resins of the methylated types 1 and 2 is low in the absence of catalyst and high in the presence of a strongly acidic catalyst, the mechanism whereby the melamine-formaldehyde resin is enriched in the paint film surface is postulated as described below. The mechanism is illustrated in **Fig. 8**.

1) When the paint film is heated, the blocking agent amine is dissociated from the acidic catalyst.
2) Since the dissociated amine tends to vaporize near the paint film surface, the active acidic catalyst concentration increases in the paint film surface. On the other hand, since the dissociated amine is less liable to go out of the system in the bulk of the paint film, the active acidic catalyst concentration becomes lower than in the paint film surface.

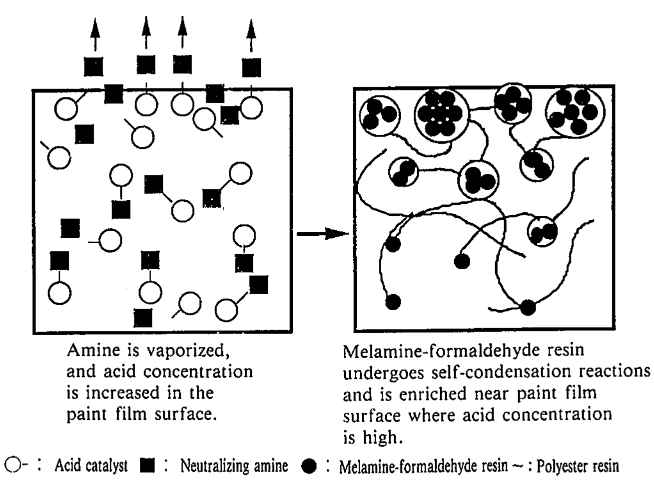


**Fig. 8** Mechanism of formation of melamine-formaldehyde resin enriched layer in paint film surface

3) For the reason noted above, the self-condensation reaction of the melamine-formaldehyde resin tends to occur near the paint film surface, and a crosslinked layer is formed by the self-condensation of the melamine-formaldehyde resin.
4) As the melamine-formaldehyde resin is consumed near the paint film surface, the melamine-formaldehyde resin in the bulk of the paint film is diffused to the paint film surface.
5) A melamine-formaldehyde resin-enriched layer is thus formed near the paint film surface.

When melamine-formaldehyde resin of the methylated type 1 or 2 is used, the catalyst is active and high in acidity also in the bulk of the paint film if not blocked by amine, which facilitates the self-condensation reaction to the detriment of melamine-formaldehyde resin enrichment toward the paint film surface. Melamine-formaldehyde resins of the imino type and partially methylated type undergo the self-condensation reaction in the absence of catalyst under the baking conditions of paints for prepainted steel sheet. As a result, the melamine-formaldehyde resin is considered to undergo the self-condensation reaction irrespective of the type of catalyst, and therefore does not enrich in the paint film surface.

The melamine-formaldehyde resin enrichment in the paint film surface does not take place with the polyester resin C of high hydroxyl value. This may be explained as follows. The reaction between the hydroxyl group of polyester resin and the functional group of melamine-formaldehyde resin is so active that the melamine-formaldehyde resin reacts with the polyester resin in the bulk of the paint film before it can come out to the paint film surface.

The increase in the melamine ring carbon concentration in the paint film surface with the increase in the catalyst content of the paint film may be interpreted as a result of the self-condensation reaction of melamine-formaldehyde resin in the paint film surface. The melamine ring carbon concentration is obtained from the area ratio of the CN spectrum to the C1s spectrum. When the self-condensation reaction of melamine-formaldehyde resin proceeds, compounds containing carbon, oxygen and hydrogen atoms, such as alcohol and aldehyde, are desorbed, and the nitrogen concentration becomes relatively high. Although the number of melamine rings is constant, the area ratio of the CN spectrum increases as the self-condensation reaction of melamine-formaldehyde resin proceeds. When the self-condensation reaction of melamine-formaldehyde resin proceeds near the paint film surface, the diffusion of melamine-formaldehyde resin from the bulk to the paint film surface is believed to increase the number of melamine rings. Which factor has a larger impact on the spectral change is not known here.

## 4. Development of Prepainted Steel Sheet with Excellent Formability and Stain Resistance

As evident from **Figs. 6** and **7**, the technology reported here can combine formability and stain resistance. Hardness can be raised as well as stain resistance. According to these findings, the type of polyester resin, type of melamine-formaldehyde resin, proportions of polyester and melamine resins, and type and content of catalyst were studied for their effects in various ways. As a result, a new type of prepainted steel sheet, trade named Viewkote IV, was commercialized. In **Table 4**, the properties of Viewkote IV are compared with those of conventional prepaint-

**Table 4** Properties of new type of prepainted steel sheet (trade named "Viewkote IV")

| Type of Viewkote | | | Formability | | Stain resistance | Hardness | 24-h immersion in 5% NaOH aqueous solution | 24-h immersion in 5% aqueous solution of sulfuric acid | Gloss |
|---|---|---|---|---|---|---|---|---|---|
| | | | 20°C | 0°C | Black marking ink | Scratch | | | |
| New | Multi-purpose type | IV | 0T | 3T | Excellent | H | Acceptable | Acceptable | 93 |
| Conventional | High-formability type | I | 0T | 4T | Poor | HB | Acceptable | Acceptable | 83 |
| | Balanced type | II | 3T | 8T | Fair | F | Acceptable | Acceptable | 82 |
| | High-stain resistance type | III | 5T | —— | Good | H | Acceptable | Acceptable | 84 |

ed sheet products Viewkote I to III. Viewkote IV is characteristic in that it has formability higher than Viewkote I, combines high formability with hardness and stain resistance equal or superior to levels of Viewkote III, and is high in gloss as well. Its chemical resistance is comparable to that of the conventional high-formability type Viewkote I. Viewkote IV is currently used in many applications, including washing machines, outdoor air conditioner units and refrigerators, contributing toward the expansion of the prepainted steel sheet demand.

## 5. Conclusions

(1) When a polyester resin of low hydroxyl value is combined with a strongly acidic catalyst blocked with amine and a melamine-formaldehyde resin with the rate of self-condensation reaction being low in the absence of catalyst and high in the presence of a strong acid, a melamine-formaldehyde resin-enriched layer is formed in the paint film surface. This mechanism has been discussed from the point of view of catalyst activity near the paint film surface in the baking process and of the self-condensation of melamine-formaldehyde resin.

(2) There is a positive correlation between the stain resistance of a paint film composed of polyester and melamine-formaldehyde resins and the melamine-formaldehyde resin concentration in the paint film surface. This is probably because the self-condensate of the melamine-formaldehyde resin enriched in the paint film surface improves the stain resistance of the paint film.

(3) On the basis of these findings, a new type of prepainted steel sheet that is bendable to 0T at 20°C and has excellent hardness and stain resistance, was developed and commercialized under the trade name "Viewkote IV".

### References

1) Kanai, H., Oka, J., Nomura, H.: Preprint of Spring Meeting of the Spectroscopical Society of Japan, 1991, p.7
2) Kanai, H. et al.: CAMP-ISIJ. 6, 1494 (1993)
3) Nomura, M. et al.: CAMP-ISIJ. 3, 574 (1990)
4) Mitsui-Cyanamid technical brochure
5) Ikishima, K. et al.: Journal of the Japan Society of Colour Material. 64 (12), 780 (1991)