Technical Report

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Development of ZINKOTE™ COLOR

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Abstract

As the housing material of home appliances, and OA and electronic equipments, the black thin-film coating steel plate "Standard Black", which is a green product produced in a cost-effective manner to obtain excellent surface properties, was developed. It was accomplished with the water-based paint which is environment-friendly and able to carry out energy-saving coating, and with development of noble water-based resin as the paint component and improvement of black pigment processing. Furthermore, new conductive particles was investigated and applied to the coating of "Standard Black", and "Conductive Heat-Absorbing Black" was developed. On the other hand, "Scratch-Resistant Black" and "Scratch-Resistant Silver" with superior scratch resistance to "Standard Black", and then "Standard White" with whole opaque white color and excellent covering ability over under-surface, were developed. These new products can be used as the home appliances, OA, electronic equipments, and so on.

1. Introduction

For many housings of flat-panel TVs, DVDs, office automation equipment, air conditioners, washing machines, carborne devices, and lighting apparatuses, a pre-coated steel sheet (e.g., VIEWKOTE™ of Nippon Steel & Sumitomo Metal Corporation) that does not require coating the housings after fabrication is used. A pre-coated steel sheet is manufactured by applying a solvent-based paint onto a chemically processed steel sheet to form a two-layer resinous film (undercoat + decorative coat), 10 μm or more in thickness, which improves the appearance, formability, and surface properties of the steel sheet.

On the other hand, with the decline in prices of home appliances and office automation equipment in recent years, there is a growing need for low-cost steel materials. At the same time, so-called green products, which help save energy and are environmentally friendly, are increasingly desired.[1)] Under these conditions, it has become necessary for steelmakers to supply new steel sheets that are comparable in appearance, formability, and surface properties to conventional pre-coated steel sheets; are less expensive than pre-coated steel sheets; and emit very small amounts of volatile organic compounds (VOCs) and CO_2 during the manufacturing process. Therefore, Nippon Steel & Sumitomo Metal is developing a new thin-film-coated steel sheet using a water-based paint that is more environmentally friendly than the conventional solvent-based paint. The company began with structural design of a water-based film binder resin and improvements in the technology for dispersing a black pigment in the binder resin with the aim of developing black film-coated steel sheets. By applying the newly developed paint in-line onto a chemically treated steel sheet to obtain a black resin-based film several μm in thickness, the company came up with "Standard Black" and "Conductive Heat-Absorbing Black," both of which are inexpensive green products with high performance.

Next, by increasing the thickness of the resin-based film on a chemically treated steel sheet to approximately 10 μm, the company could obtain new steel sheets that have excellent scratch resistance and a new white film capable of making the base metal color almost indiscernible. In addition to the design of the abovementioned film binder resin, studies on the addition of hard scratch-resistant resinous beads and on the prescription of a pigment for enhancing the color hiding capability, conducted on the basis of a solvent-based paint, made it possible to develop higher-order products having high functions—"Scratch-Resistant Black," "Scratch-Resistant Silver," and "Standard White."

This technical report focuses on the film technology involved in the Standard Black and Conductive Heat-Absorbing Black. It also

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provides information about the technology relating to the higher-order high-function products.

2. Development of the Standard Black

2.1 Solution of problems with water-based paint and development of film

Table 1 compares the characteristics of solvent-based (Please replace the term "Solvent-processed" by "Solvent-based" and the term "Waterborne" by "Water-based" in Table 1, Table 3, and Fig. 10) paint and conventional water-based paint used for the coating of steel sheet.

The viscosity of the water-based paint under low shear rate or in a stationary state is only 1/20 to 1/5 that of the solvent-based paint. It is as low as the viscosity of soy sauce or orange juice at normal temperature. At most, the viscosity of the paint is not higher than that of olive oil. Therefore, unlike the solvent-based paint film on pre-coated steel sheet, the water-based paint cannot be applied very thick. Even when the paint is added with a coloring pigment, it can hardly make the base metal color indiscernible. Moreover, when the viscosity of the paint is low, the pigment added settles fast and is not dispersed well.

Furthermore, when the film obtained with the conventional water-based paint is compared with the film obtained with a solvent-based paint, the binder resin has a low degree of cross-linking and inferior water resistance, and the invasion of corrosive ions and separation of film tend to occur easily. In many cases, the film has insufficient corrosion resistance. Because of the low cross-linking degree, the film coagulation force also tends to become insufficient, making the film adhesion during the processing insufficient. Therefore, it is difficult to secure desired surface properties of steel sheet, including appearance and corrosion resistance, in the film obtained with the conventional water-based paint.

Table 1 Characteristics comparison between solvent-based and water-borne paint

			Solvent-based paint	Water-based paint
Paint viscosity at low shear rate			High	Low
	Thick film forming, covering over undersurface		Better	Worse
	Pigment dispersibility		Better	Worse
Water resistance			Superior	Inferior
	Corrosion resistance		Better	Worse
Painting process	Drying temperature		High	Low
		Production efficiency	Low	High
		CO_2 discharge limitation	Inferior	Superior
	Environmental burden		Large	Small
		VOC discharge limitation	Inferior	Superior

On the other hand, in the coating process using a water-based paint, it is possible to dry the paint and form the film at a lower temperature and in a shorter time than in the coating process using a solvent-based paint. Thus, the coating process using a water-based paint consumes less energy and emits less CO_2. In addition, the water-based paint produces very small amounts of VOCs and has less impact on the environment than the solvent-based paint.

In view of the above characteristics of water-based paint, we re-examined the types of film binder resins for conventional water-based paint, reviewed the principal chain structure of resins, redesigned the type and number of polar functional groups to be introduced to the resin chain, and introduced a new hardening agent with to increase the resin cross-linking degree (film density) by speedy paint drying/film forming at a low temperature and securing a good balance between corrosion resistance/chemical resistance and paint adhesion, which are ordinarily incompatible with each other. As a result, we could secure the required surface properties even when the number and thickness of layers of the resin-based film were smaller than those of the conventional pre-coated steel sheet. In addition, among several inexpensive carbon-based black pigments having high hiding power, we selected one that could exist stably in a water-based paint containing the abovementioned binder resin, so that particles of the pigment 50–500 nm in size would be evenly dispersed throughout the film. As a result, as schematically shown in **Fig. 1**, we could develop the Standard Black—a new black thin-film-coated steel sheet having high hiding power and good surface properties with a single layer of film 3–4 μm in thickness as compared with the conventional pre-coated sheet with two layers of film about 10 μm in thickness.

2.2 Visible light absorption mechanism of the Standard Black film

Figure 2 schematically shows the condition of existence of the black pigment dispersed in the Standard Black resin-based film. Many primary particles of the black pigment 10–100 nm in size comprise aggregates having a microscopically irregular surface structure 50–500 nm in size, which are evenly dispersed in the film. Since the wavelength (380–780 nm) of the visible light entering the film is nearly the same as the size of concaves in the microscopically irregular structure, the visible light enters these concaves where it is subject to multiple scattering. Before the incident visible light can leave the film, it is mostly absorbed by the mechanism described below. Since many aggregates

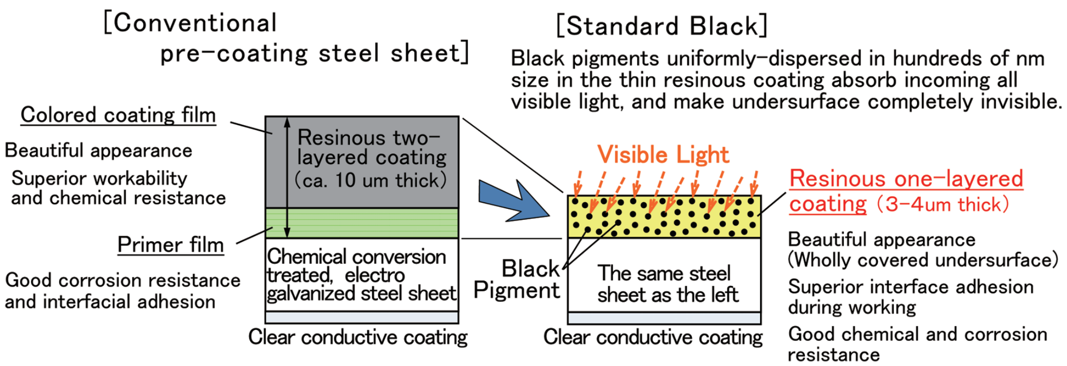

Fig. 1 Cross-section structure of conventional pre-coating steel sheet and Standard black

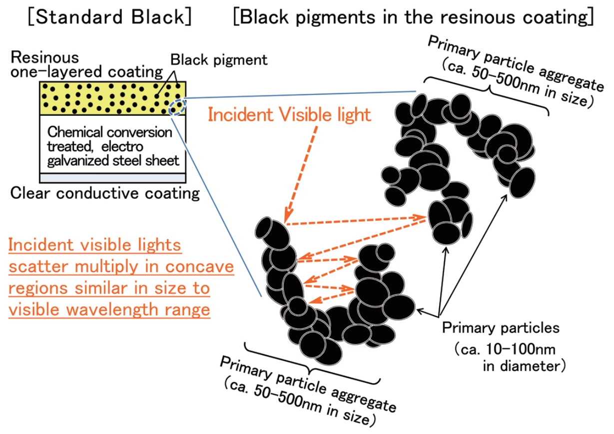

Fig. 2 Visible light absorptioin into black pigment in the course of its multiple scattering process

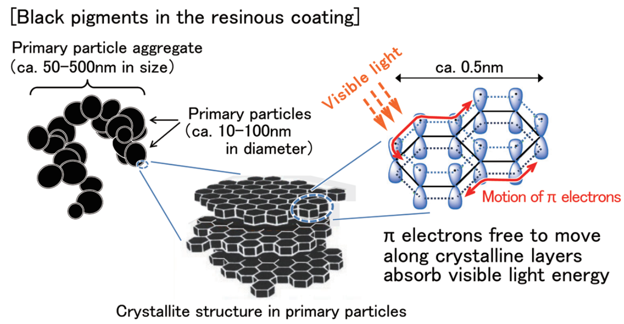

Fig. 3 Visible light absorptioin by π electrons in black pigment

of primary particles are present in the film, and the individual aggregates have a complicated irregular structure, the total surface area of pigment particles is sufficiently large to enhance the scattering of light and efficiency of light absorption.[2, 3]

The visible light absorption mechanism of black pigment in the film is shown in **Fig. 3**. On the crystalline structure composed of primary particles, there are π electrons that move freely along the layers of crystal. Those π electrons easily absorb the energy of visible light and are highly energized (π-π^* transition). The absorbed energy is dissipated into the film in the form of heat, and the energy of π electrons declines to the original level.

3. Development of the Conductive Heat-Absorbing Black

3.1 Need for conductive, heat-absorbing steel sheet

Home appliances, office automation equipment, and carborne electronic devices require grounding their housing to protect the internal electronic parts as well as the owner from dangerously large electric currents. In addition, from the standpoint of preventing malfunctioning of electronic parts because of the entry of electromagnetic waves into the housing and avoiding adverse effects on peripheral devices because of the leak of electromagnetic waves to the outside of the housing, the housing is required to be capable of shielding electromagnetic waves (EMC: electromagnetic compatibility). The steel sheets used for housings are electrically conductive and have grounding capability and EMC. However, when a housing cabinet is made from a steel sheet with an insulating film, the joints of members contact on their film surfaces, breaking the electromagnetic shield.

In order to effectively shield high-frequency electromagnetic waves (10 MHz to several GHz) from home appliances, office automation equipment, and cell phones, it is necessary to keep the length of each long nonconductive joints within 1/10 (several mm) of the wavelength of the electromagnetic wave under consideration. In many cases, a nonconductive joint is made conductive by applying a conductive packing (EMC gasket/shield line) as shown in **Fig. 4** [4] and an EMC conductive tape. However, since the use of conductive packing to secure EMC requires extra cost, a surface-treated steel sheet free of nonconductive joints of film is desired.

In the case of home appliances, the temperature inside the housing tends to rise because of the heat generated by internal electronic parts (circuit boards; includes the luminous panel and backlight for TVs). Since an excessive temperature rise can cause a malfunction of electronic parts, radiators (radiating plate, sheet, and fan) made from a highly conductive metal (aluminum and copper) are incorporated in home appliances. Examples of radiating parts built in a flat-panel LC TV are shown in **Fig. 5**.

With the decrease in thickness and size of home appliances in recent years, the number of radiating parts required to lower the temperature inside the housing are increasing, causing the cost of manufacturing to increase. Moreover, it has become increasingly difficult to secure space for additional radiator parts within thin, small housings. Under these conditions, reducing the number of radiator parts is an important challenge to every manufacturer of electronic equipment. Thus, there is strong need for a new steel sheet for housing that permits radiating the internal heat easily.

3.2 Utilization of the Standard Black film

In developing a new steel sheet that meets the abovementioned requirements, we considered utilizing the inexpensive yet high-performance Standard Black film to minimize the development period.

Figure 6 shows the mechanism by which an electronic device housing that is capable of absorbing heat efficiently dissipates heat from the inside of the housing to the outside. The heat generated from the circuit board (heat source) is absorbed by the rear side of the housing and dissipated to the outside from the front. The emissivity, which can be measured with a radiation thermometer, is used as an indicator of the efficiency of heat absorption/radiation. Namely, the higher the

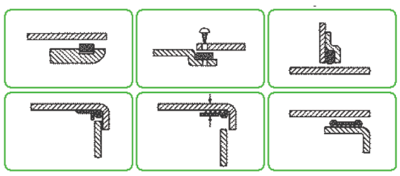

Fig. 4 Example schemes of use of electromagnetic shielding gaskets to equip nonconductive joints with electromagnetic compatibility [4]

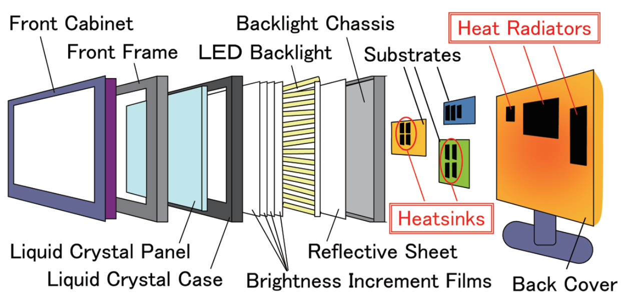

Fig. 5 Scheme of flat-screen liquid crystal display TV and heat radiators

emissivity, the higher is the efficiency of heat radiation (i.e., the temperature inside the housing can be lowered more efficiently).

Table 2 compares the principal means of heat radiation (radiating plate, cooling fan) for home appliances, office automation equipment, and electronic devices with the Standard Black in terms of thermal properties and productivity. The Standard Black has high emissivity. It also has an advantage over the radiating plate and cooling fan for the housing to easily be reduced in thickness and mass-produced, and in the cost of manufacturing. Therefore, the development of a conductive heat-absorbing steel sheet was studied by introducing a conductive pigment into the Standard Black film without impairing its high emissivity.

3.3 Infrared ray absorbing mechanism of the Standard Black film

Figure 7 schematically shows the condition of dispersion of the aggregates of black pigment in the Standard Black film. The far-infrared ray (heat ray) emitted from a certain object at a certain temperature has a wide wavelength. Using Wien's formula, the peak wavelength of infrared rays emitted from an object whose temperature is in the range 30°C–100°C can roughly be calculated to be 7–10 μm. Far-infrared rays whose wavelength is 0.5–3 times of the peak wavelength [5] enter aggregates of the black pigment dispersed in the film and are subject to multiple scattering. As a result, they are mostly absorbed by the film before they can leave the film. Since the aggregates have a large total surface area, they scatter and absorb light efficiently.[6-8]

On the other hand, a water-based film binder resin contains many infrared-active polar functional groups. When far-infrared rays pass through the resinous binder, infrared rays of specific frequency contained in the far-infrared rays induce a deformation vibration, whereby the bond angle of atoms making up the functional groups is widened and narrowed periodically, and an asymmetric stretching vibration, whereby the distance between different types of atoms, is asymmetrically changed.[9]

The energy of infrared rays absorbed after multiple scattering and molecular vibration is transformed into internal heat and dissipated into the film. In the case of a housing, as shown in Fig. 6, the internal heat of the reverse-side film reaches the front-side film through conduction and is transformed into a far-infrared ray having a wavelength appropriate to the film temperature and dissipated to the outside of the film.

3.4 Study on making the film conductive

Figure 8 schematically shows the two methods that are generally used to impart conductivity to a resin-based film. In (a), metallic particles of Ni, Zn, and Al are introduced to the film as the points of conduction. In the case of a water-based paint, this method cannot be applied because the metallic particles corrode easily. In (b), a metallic sheet (e.g., chemically treated steel sheet) is provided with microscopic irregularities and, the resulting convex parts, where the resin-based film is small in thickness, are used as the points of conduction. With this method, high emissivity and adequate corrosion resistance cannot be secured because the film on the convex parts becomes extremely small in thickness. Therefore, we tested more than 100 types of organic and inorganic conductive particles. As a result, we could

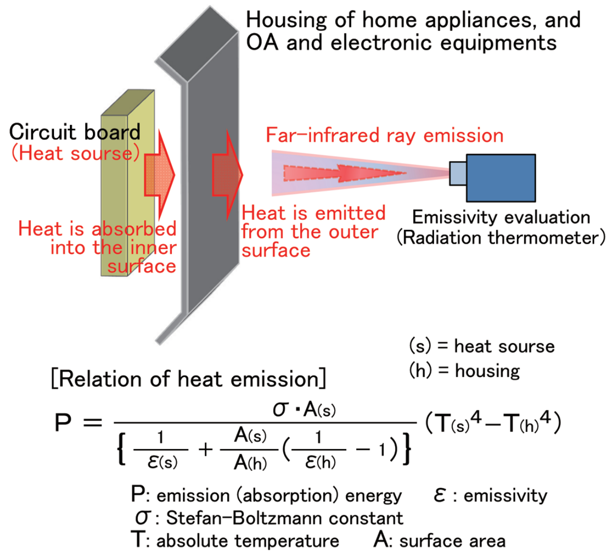

Fig. 6 Heat emission by well heat-absorbable housing

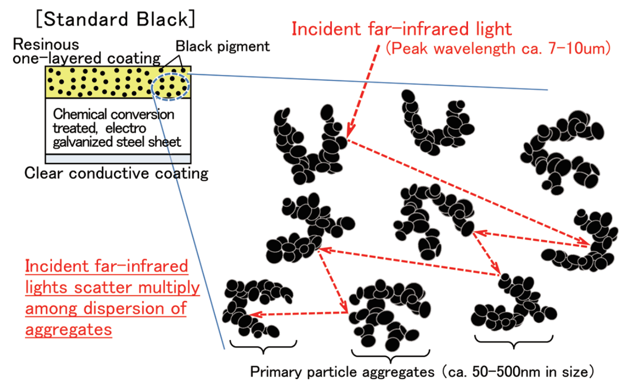

Fig. 7 Far-infrared absorptioin into black pigment in the course of its multiple scattering process

Table 2 Comparison of thermal property and productivity among means of heat radiation by heat conduction, convection and emission

			Heat conduction		Convention	Emission
			Aluminum (heatsink)	Copper (heatsink)	Cooling fan	Standard black
Thermal property	Emissivity (= absorptivity) (%)	Surface	3–5	3–4	—	70–75
		Rear surface	3–5	3–4	—	15
	Heat conductivity (100°C, W/m · K)		240	395	—	54–62 (mild steel)
Productivity	Response to compactification		Difficult	Difficult	Difficult	Easy
	Mass productivity		Inefficient	Inefficient	Inefficient	Efficient
	Production cost		Expensive	Expensive	Reasonable	Inexpensive

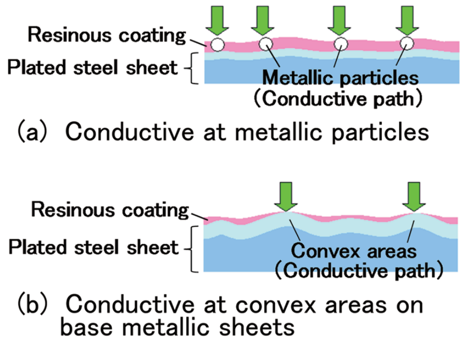

Fig. 8 Conventional methods to equip coating with conductive property

find conductive particles that exhibited long-time water resistance, good dispersibility and retention capacity in water-based paint, and they were as economical as the metallic particles used in Fig. 8 (a).

To introduce the above particles to the Standard Black film, we optimized the paint composition and film specifications. Thus, the conductive heat-absorbing black featuring high emissivity and good conductivity could be developed.

3.5 Conductivity and heat absorbing/radiating performances of the Conductive Heat-Absorbing Black

The conductivity of the Conductive Heat-Absorbing Black is on a practical level. When measured by the four-terminal, four-point probe method, the contact resistance at the film surface that is used as the leading index of conductivity by many manufacturers of home appliances and office automation equipment was less than 1 mΩ, which is considered to allow good grounding performance and EMC.

The heat absorbing/radiating performances were evaluated using a heat box that simulated the housing of a home appliance, as shown in **Fig. 9**.[10] Four types of surface-treated steel sheets were used for the performance evaluation. They were as follows: (1) solvent-based, heat-absorption black film coated steel sheet (thickness of resin-based black paint film: about 20 μm on front side and about 3 μm on reverse side), (2) Conductive Heat-Absorbing Black (thickness of resin-based black paint film: about 3 μm on both sides), (3) Standard Black (thickness of resin-based black paint film: about 3 μm on front side; clear conductive film on reverse side), and (4) clear conductive film-coated steel sheet (clear conductive film on both sides). With each of the four samples set on top of the heat box, the interior of the heat box was heated by a heater for 100 min. Then, the change in internal temperature till the thermal equilibrium was almost reached was compared. The measurement results are shown in **Fig. 10**. When the Conductive Heat-Absorbing Black was applied, the temperature inside the housing after the thermal equilibrium was almost reached was much lower than that when the Standard Black or clear conductive film-coated steel sheet was applied, whereas it was nearly the same as that when the solvent-based, heat-absorption black film coated steel sheet with a thick film was applied.

The reason why the Conductive Heat-Absorbing Black lowers the temperature inside the heat box more effectively than the Standard Black lies in the difference in the heat-absorbing capacity of the reverse-side film, which receives heat from the heater installed in the heat box. The black film on the reverse side of the Conductive Heat-Absorbing Black has higher emissivity than the clear conductive film on the reverse side of the Standard Black. By Kirchhoff's law, under a thermally equilibrium state, emissivity is equal to absorptivity. Therefore, the reverse side of the Conductive Heat-Absorbing Black has larger heat-absorbing capacity. It is evident from the heat radiation

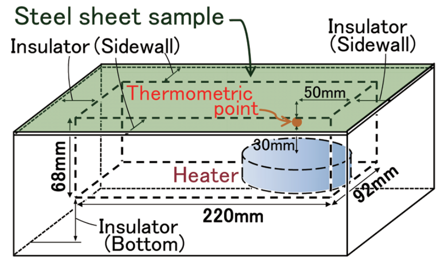

Fig. 9 Model to simulate warming inside home appliance housing[10]

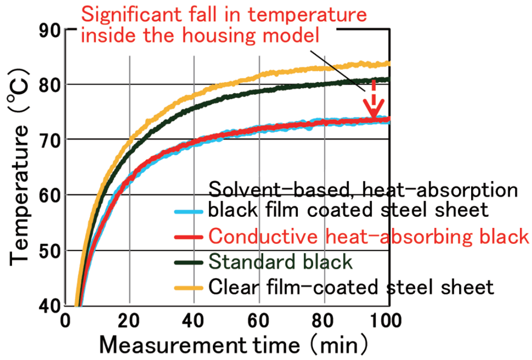

Fig. 10 Temperature changes inside the simulated housing model of home appliance over heating time

relation that a film having higher emissivity has larger heat-absorbing capacity. Namely, in the equation given in Fig. 6, as the housing emissivity ε(h) approaches to emissivity of a black body (approximately 1), the denominator of the right side decreases, and the absorbed energy P increases.

4. Development of Higher-Order, High-Performance Steel Sheets

The types of ZINKOTE™ COLOR are shown in **Table 3**. With the Standard Black, a resin-based thin film several μm in thickness obtained from a water-based paint does not always provide sufficient scratch resistance. Therefore, we also developed "Scratch-Resistant Black." Specifically, the scratch resistance of the resinous film binder was improved by a solvent-based paint while directly utilizing the technology incorporated in the Standard Black. In addition, the film was made thicker than that of the Standard Black, and resin beads harder than the resinous binder were mixed in the film. As a result, a high degree of scratch resistance could be attained. The hard resinous beads helped reduce the area of contact between the film and mold surface during pressing, thereby enhancing the scratch resistance of the film.

Similarly, "Scratch-Resistant Silver" was successfully developed. With a solvent-based paint used as the base, the new scratch-resistant steel sheet was developed through the improvement of the resinous paint binder, addition of hard resinous beads, and design of a thicker paint film. Taking advantage of the excellent hiding power of silver coloring pigment, we also developed "Standard Silver" with a thin silver film on the basis of a water-based paint.

Unlike the black and silver types, the white type, which also enjoys considerable demand, had the problem of poor hiding power because of its thin white film obtained from a water-based paint. Therefore, we designed a thicker film based on a solvent-based paint and studied the prescription of a white pigment for enhancing the hiding power.

Table 3 Lineup of several types of ZINKOTE™ COLOR

Color	Type	
	Thin film type (water-based)	More functional (solvent-based)
Black	Standard black	Scratch-resistant black
	Conductive heat-absorbing black	—
Silver	Standard silver	Scratch-resistant silver
White	—	Standard white

As a result, we could develop "Standard White" that secures whiteness of practical level.

Through the development of higher-order, high-performance steel sheets, the scope of application of ZINKOTE™ COLOR has been continually expanded. In addition, we have plans to develop new types of steel sheets having new functions that enhance the comfort and ease of use of steel sheets.

5. Conclusion

As materials for the housings of home appliances, office automation equipment, and carborne electronic devices, we developed the Standard Black—a black-colored "green product" that is economical and has good surface properties—by using an environmentally friendly, water-based paint, and by studying resinous binders and prescription of black pigment. In addition, we developed the Conductive Heat-Absorbing Black by introducing new conductive particles to the Standard Black film. Furthermore, the "Scratch-Resistant Black" and "Scratch-Resistant Silver"—higher-order steel sheets having excellent scratch resistance—were developed. The Standard White having adequate whiteness and hiding power has also been developed.

Since all these steel sheets are cost-effective with high performance, it is expected that they will find a wide scope of applications including the housings of home appliances and office automation equipment.

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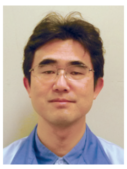

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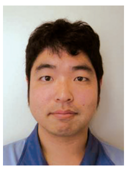

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