

Research on Photo-degradation Behavior of E-coat

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ABSTRACT

An automotive paint process that remove the primer process has been developed in order to reduce the energy consumption and CO₂ emissions. An analysis method of the photo-degradation of the E-coat when the primer is removed was established, based on the changes in physical properties and chemical structures. As a result, the range of wavelength that cause peeling potential is under 550 nm. Based on these results, a layer to shield under 550 nm of light (1 base) was applied before the color development layer (2 base) without the drying process, enabling elimination of the primer process without limitation to color development.

1. Introduction

Recently, the need for the reduction of manufacturing energy costs and CO₂ emissions has been increasing, along with shortening of the automotive paint process. Conventionally, the application of body paint has mainly involved a four-coat/three-bake (4C3B) process, in which an E-coat is applied, after which a primer is applied and cured, following which a color base coat and a clear coat are applied and cured. Today, the use of a four-coat/two-bake (4C2B) process is becoming more widespread⁽¹⁾. This process shortens the curing process from the primer process, with the topcoat being applied following drying of the primer. In addition, from around 2004, a three-coat/two-bake (3C2B) process began to be applied among European manufacturers. This process removed the primer process, and applied the topcoat following the application of the E-coat (Fig. 1). However, removing the primer process means that the light-shielding function fulfilled by the primer is also lost. As a result, the behavior of light transmission to the E-coat changes for each color, increasing the potential for peeling of the topcoat due to

photo-degradation of the E-coat. This situation causes limitations on the color variations that can be developed. The research discussed in this paper therefore analyzed the photo-degradation behavior of the E-coat due to light transmission, and formulated a paint content able to reconcile the ability to remove the primer process with the ability to use a broader range of color variations. The details of the research are reported below.

2. Paint Quality Issues in the Removal of the Primer

Figure 2 shows the layers applied in the standard coating process, and Table 1 shows the role of each layer. The body paint is an E-coat applied to the steel sheets, which has the function of protecting the body from corrosion. The primer is applied to the E-coat for light shielding and stone chip resistance. After the base coat, which provides the color, the clear coat, which offers smoothness and weather durability, are applied. When the primer is removed, the functions that it conventionally fulfills are also lost. Because the qualities change for color

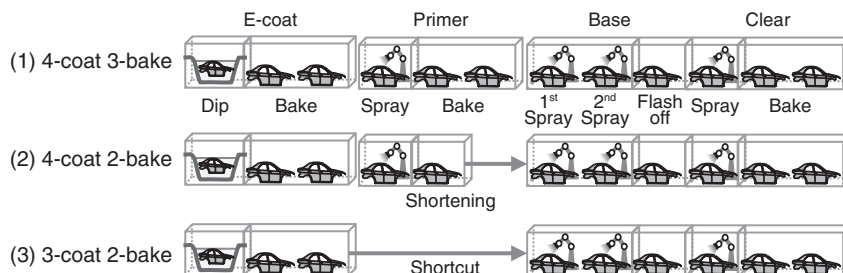


Fig. 1 Paint process of automobile

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Table 1 Function of each layer

Layer	Function
Clear	Appearance, Weather durability
Base	Coloring
Primer	Light interception, Chip resistance
E-coat	Corrosion control

changes such as hue and brightness, and their behavior with respect to absorption or transmission of light therefore changes, light transmission to the E-coat also changes with the removal of the primer. Figure 3 shows this effect. Light transmission behavior is dependent on the light absorption characteristic of the pigments in the base coat. White shows a low level of absorption for all wavelengths of visible light, and therefore transmits light easily, while black shows a high level of absorption for all wavelengths, and thus transmits almost no light. The chromatic color blue absorbs comparatively long wavelength from visible light, but is unable to absorb short wavelength, and they therefore tend to be transmitted to the E-coat. Light transmission is also affected by the film build, and thin films are not able to fully shield light rays. Because of this, when the primer is removed, the transmission of light to the E-coat is dependent on the pigments in and the film build of the base

coat that provides each color. In terms of weather resistance, the E-coat is particularly prone to photo-degradation⁽²⁾, and it is therefore necessary to limit the brightness and chroma of the base in order to stably shield the E-coat from light. In concrete terms, because the brightness L^* value of general white pearl is around 90, to help ensure that the E-coat is stably shielded from light rays by the base coat only, it is necessary to reduce the brightness L^* value of the base coat to between 75 and 80 through the addition of black or similar pigments that absorb more effectively. In order to maintain a high level of brightness, it is necessary to increase the thickness of the base coat, but this causes issues such as popping and sagging easily during application. The current project studied the photo-degradation behavior of the E-coat first, and discussed the method that would be able to achieve and maintain color variations.

3. Analysis of Photo-degradation of E-coat

3.1. Conditions of Photo-degradation

The main binder of the E-coat is generally an epoxy resin containing a bisphenol group. As Table 2⁽³⁾ shows, the binder includes a variety of chemical bonds; the dissociation energy of these bonds is within the range of the irradiant energy of ultraviolet light, and the binder is therefore considered to be degraded by irradiation of UV light. Degradation of the surface of the epoxy resin due to the incidence of light of wavelengths of between 300 and 800 nm has been reported⁽⁴⁾, but it is still not known which wavelength affect degradation.

The research first studied what kinds of effect the photo-degradation of the E-coat had on the automotive body paint. Panels that would allow the transmission of light to the E-coat were prepared and exposed outdoors, resulting in the type of peeling shown in Fig. 4. Figure 5 shows the results of observation of the form of peeling and elemental analysis around the areas of peeling using a scanning electron microscope (SEM). The fact that the results of elemental analysis of the areas of peeling designated α and β showed elements originating in the titanium dioxide in the E-coat demonstrated that the peeling of the topcoat occurred as a

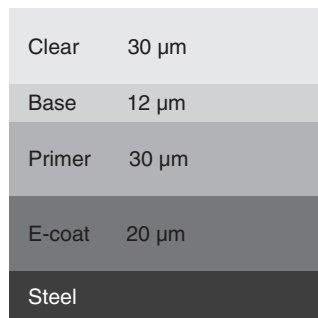


Fig. 2 Standard layer structure of body paint

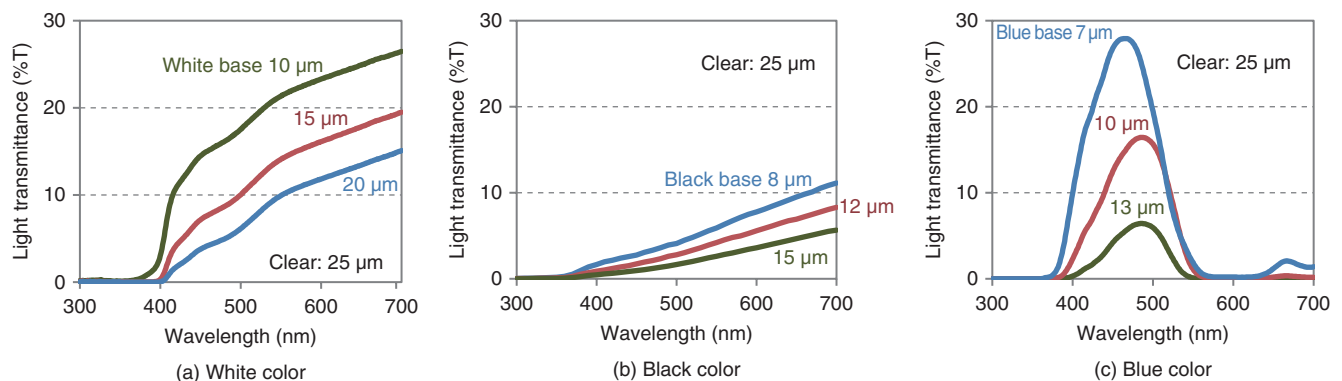


Fig. 3 Light transmittance of base and clear

Table 2 Bond-dissociation energy

Bond of E-coat	Bond-dissociation energy (kcal/mol)	Corresponding light wavelength (nm)
C-H	106	270
C-C	83	345
Ph-C	101	283
C=C	146	196
C-O	76	376
C=O	174	164
C-N	73	392
N-H	93	308
O-H	111	258

result of cohesion failure in the surface of the E-coat. This was considered to result from photo-degradation of the E-coat. In order to analyze the status of the degradation, changes in the chemical structure of the peeled areas as compared to a spare panel (a panel in the initial state)

were analyzed using a Fourier transform infrared (FT-IR) spectrophotometer. The difference spectrum between initial state and peeling areas was studied in order to determine the changes in chemical structure by the FT-IR results. The results are shown in Fig. 6. The base peak in the difference spectrum was determined at 1510 cm^{-1} , in the absorption band of the aromatic rings originating in the bisphenol resin. By comparison with the initial state, the peeled areas showed a reduction in absorption bands that could

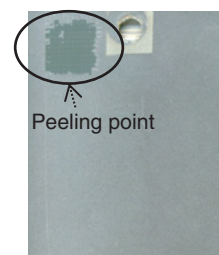


Fig. 4 Peeling of top coat after exposure test

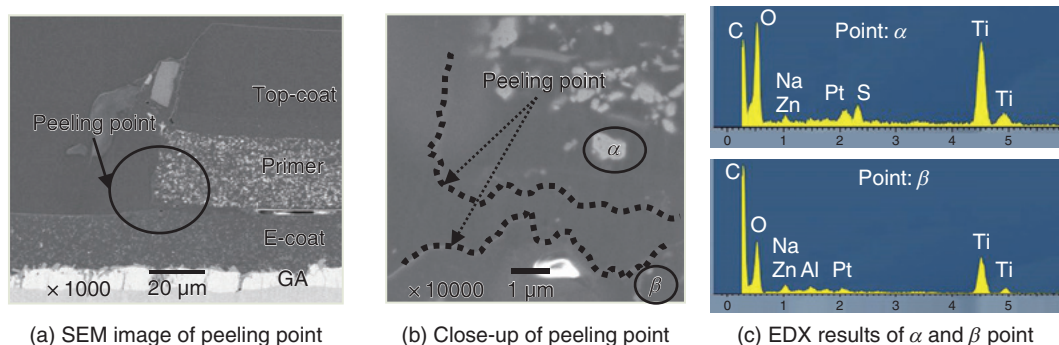


Fig. 5 Results of SEM-EDX

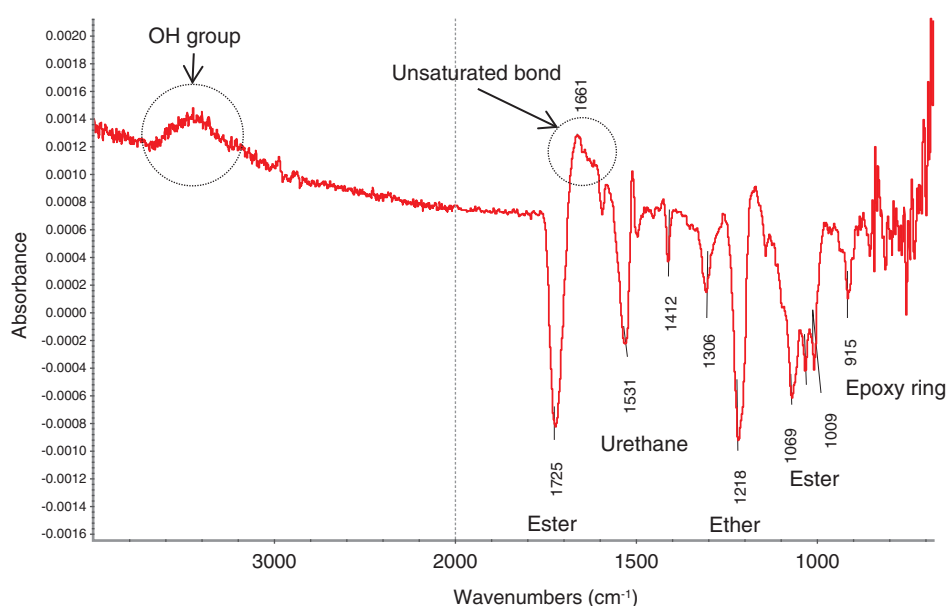


Fig. 6 Differential FT-IR spectrum of E-coat between initial sample and peeling point

be attributed to esters, urethane, and epoxy. In addition, an increase in OH groups with a peak at 3400 cm^{-1} and unsaturated bonds with a peak at 1661 cm^{-1} was observed. Based on these results, it was considered that the chemical structure of the E-coat changes due to photo-degradation, and as a result peeling occurs due to cohesion failure. Next, the wavelengths of light that degrade the E-coat were studied.

3.2. Method of Analysis of Light Wavelengths

In order to study the relationship between the wavelengths of light and the photo-degradation of the E-coat, an E-coat was irradiated in 10 nm intervals using a spectral aging testing machine. Because peeling occurs as a result of cohesion failure at the surface of the E-coat, as shown in Fig. 5(a) in Section 3.1, it was considered that photo-degradation would occur at the surface. Film strength was therefore measured at a depth of $2\text{ }\mu\text{m}$ from the surface in each irradiated area of the E-coat. It was measured using a surface and interfacial cutting analysis system (SAICAS), in order to determine the changes in physical properties due to irradiation. In addition, to provide confirmation of degradation, changes in chemical structure in each irradiated area were analyzed using FT-IR. Using these methods, it was possible to analyze photo-degradation behavior from both the physical and chemical perspectives. The panel used in the analysis was cured under the standard baking conditions at 170°C for 30 minutes. Baking conditions and inclusions of iron ions can be considered as variable elements on automotive E-coating lines, and another panel, which had been cured at 220°C for 15 minutes, the upper limit baking conditions such as the cross-linking density and physical properties of the coating, was therefore also used.

3.3. Results of Physical Analysis

With regard to the level of degradation, film strength after irradiation was expressed as a percentage, with the film strength of areas that had not been irradiated as 100. Figures of less than 100 indicated a decline in the film strength of the E-coat due to photo-degradation. Figure 7 shows the results. These results indicate that when a panel produced under standard baking conditions was irradiated by the spectral aging testing machine for 20 hours, film strength declined as a result of irradiation of wavelength of 400 nm and below. When the panel that had been cured at 220°C was tested under the same conditions, a decline in film strength was observed at wavelength of 440 nm and below, and when the irradiated time was increased from 132 to 950 hours, film strength declined for wavelength of 450 nm and below. By contrast, no decline in film strength was observed for the wavelength range above 450 nm , irrespective of irradiated time. An FT-IR spectrum for the E-coat cured at 220°C was obtained to determine the reason for this phenomenon (Fig. 8). This spectrum

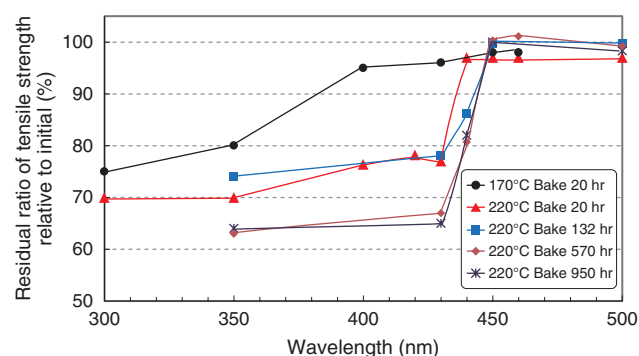


Fig. 7 Results of E-coat photo-degradation

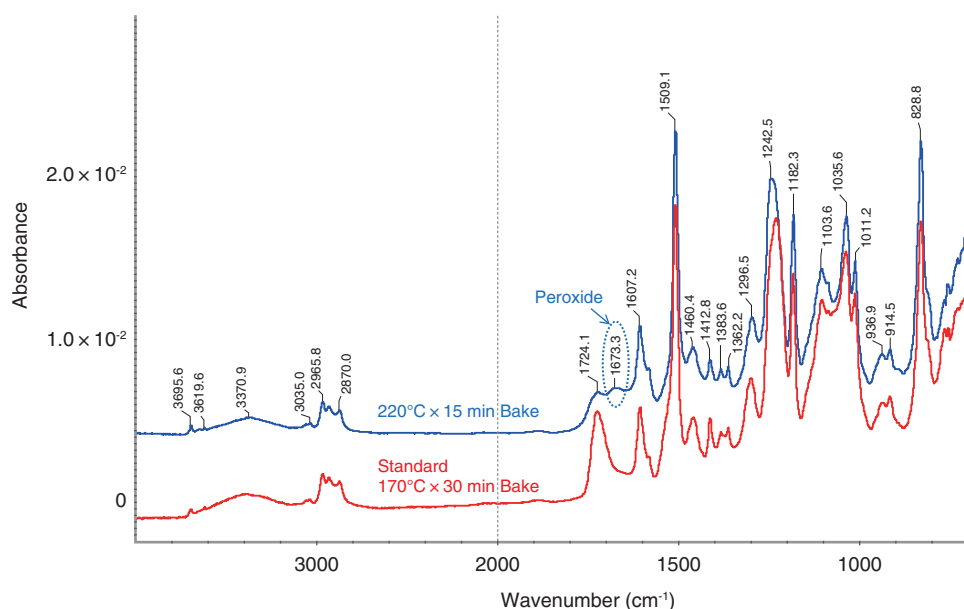


Fig. 8 FT-IR spectrum of E-coat baked at 220°C

showed a peak originating in peroxide. Because the bond dissociation energy of peroxide corresponds to a radiant energy of 447 nm⁽⁵⁾, it is considered that the dissociation of the peroxide bonds produces organic radicals, promoting a degradation reaction, with the result that a decline in film strength is observed in areas upon which light of 450 nm and below was incident.

3.4. Results of Chemical Analysis

No decline in the film strength of the E-coat was observed for wavelength of above 450 nm. FT-IR analyses were next conducted to determine whether there was any change in the chemical structure of the E-coat. Figure 9 shows the results of measurements of areas upon which each wavelength was incident following 950 hours of irradiation from a spectral aging testing machine for the panel cured at 220°C. The 1510 cm⁻¹ peak for the aromatic rings originating in bisphenol resin shows a tendency to decline at wavelength of above 450 nm. This indicates that at wavelength of over 450 nm, while there is no change in film strength, bisphenol chains in the surface of the E-coat have been subject to cleavage and have been reduced. In order to conduct a detailed study of the level of reduction of the bisphenol resin, the ratio of the areas of the 1510 cm⁻¹ peak for aromatic rings originating in bisphenol resin and the 1610 cm⁻¹ peak for aromatic rings in an area that had not been exposed to light was determined, and using this as a standard, a comparative analysis of the ratios of the areas of the 1510 cm⁻¹ and 1610 cm⁻¹ peaks for all wavelength of light for each irradiated time was conducted. The results are shown in Fig. 10. An area ratio of less than 1 on the vertical axis indicates a decline in bisphenol aromatic rings. The results show that it is wavelength of 550 nm and below at which this phenomenon occurs.

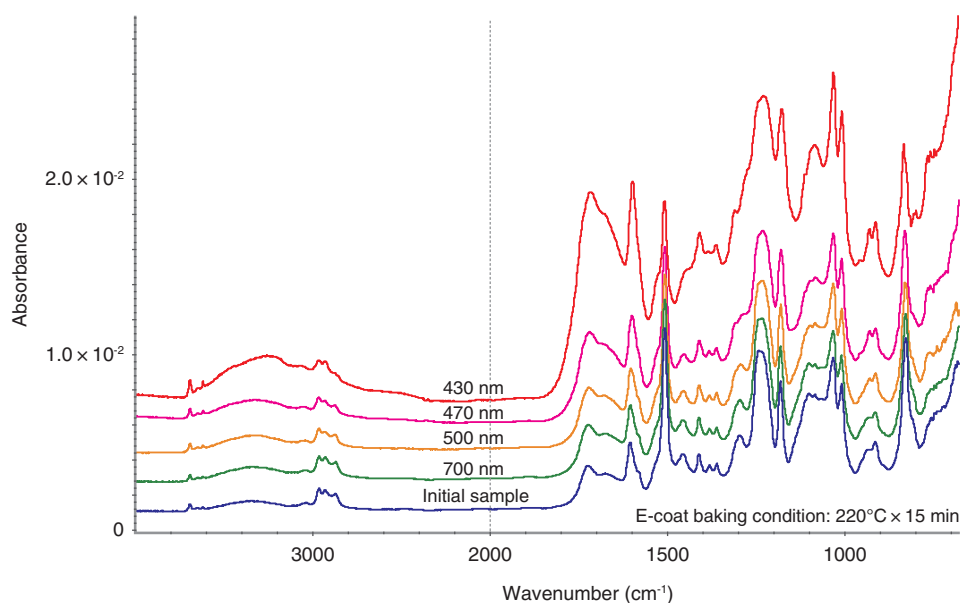


Fig. 9 FT-IR spectrum of E-coat photo-degradation (Irradiation time 950 hr)

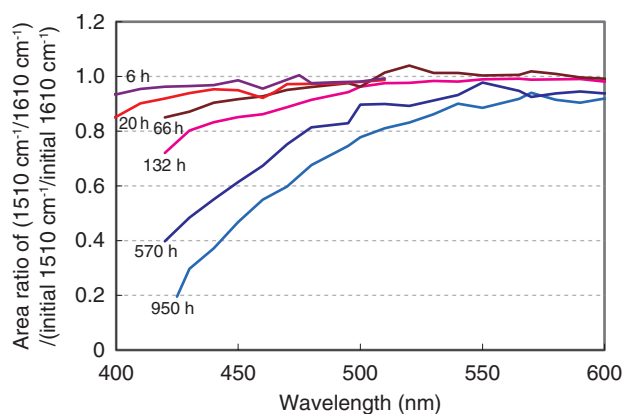


Fig. 10 Area ratio of before and after irradiation

4. Considerations

4.1. Considerations regarding Mechanism of Photo-degradation

At first it was hypothesized that photo-degradation of the E-coat occurred as a result of UV light, but the results shown in Figs. 9 and 10 indicated that the irradiation energy of visible light of wavelength between 450 nm and 550 nm also cleaves and dissociates the bonds in the binder. As causes of this phenomenon, it is possible to first consider the white pigment and corrosion inhibitor in the E-coat. However, because both are white powders, they reflect light rays of wavelength of 550 nm and below⁽⁶⁾. Carbon black is also included in the E-coat as a black pigment, but because it possesses a chemically stable structure⁽⁷⁾, it is not considered to be a point of origin for degradation. FT-IR spectra were therefore studied before and after irradiation. As Fig. 11 shows, in addition to the production of peroxide and carbonyl as a result of degradation following irradiation,

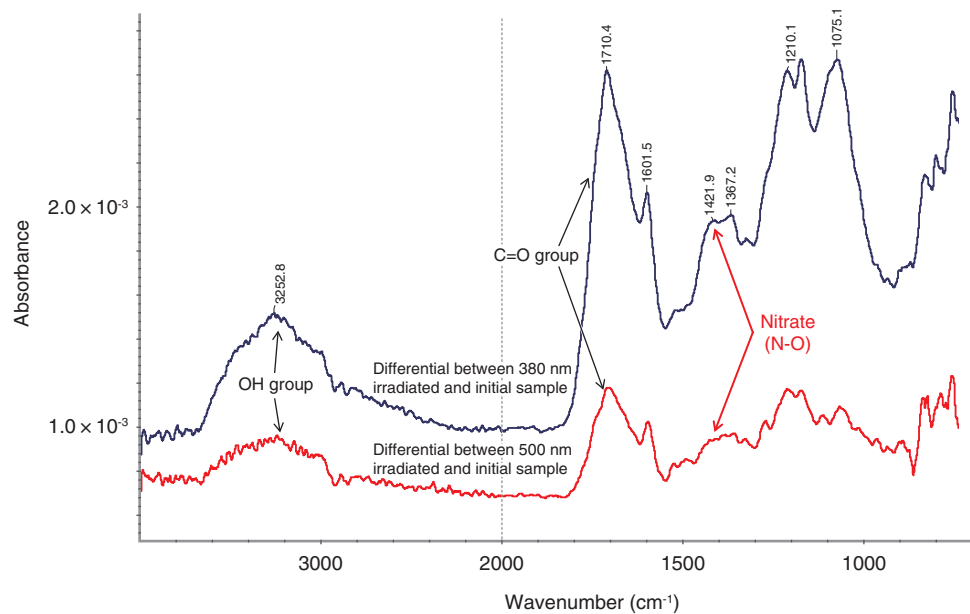


Fig. 11 Differential FT-IR spectrum of E-coat

there is also a slight peak close to 1400 cm^{-1} originating in NO_x , and this NO_x component is therefore considered to have an effect on degradation. Because NO_x is highly prone to form radicals⁽⁸⁾, there is considered to be a strong possibility that radicals produced from NO_x as a result of irradiation to visible light of between 450 nm and 550 nm could result in cleavage of the bonds in the bisphenol resin. This NO_x component is considered to become incorporated in the E-coat in small quantities as an impurity during curing.

4.2. Range of Light Wavelength That Affect Peeling

The results of the study discussed in Section 4.1. showed that light at wavelength of 450 nm and below resulted in degradation corresponding to a decline in the film strength of the E-coat, while light at wavelength of between 450 nm and 550 nm , despite the fact that no decline in film strength was observed, caused cleavage of the bonds in the bisphenol resin. While the form of degradation differs, because the peaks in areas on which light, for example of wavelength of 430 nm and 500 nm , was incident are similar (Fig. 9), it is considered that the only difference is the degree of cleavage of the bonds in the bisphenol resin. Bisphenol is the main binder of the E-coat, and it is therefore necessary to attempt to prevent its reduction by degradation. In addition, it is also considered to be necessary to intercept light of wavelength of 550 nm and below and attempt to prevent peeling of the topcoat in order to help prevent the production of the radicals that are thought to be the main factor in photo-degradation.

5. Countermeasure against Photo-degradation

5.1. Determination of Paint Content

Based on the analysis results discussed above, paint

content was formulated in which a layer that intercepted light (1 base) was situated under the color-developing layer (2 base). In designing the 1 base , the ability to stably intercept light of wavelength of below 550 nm by means of management to produce a suitable film build was an important consideration. The design therefore made it possible to intercept light using a suitable film build with wide-ranging light absorption properties, from the UV range to the visible spectrum. The 2 base can be applied after application of the 1 base , with no drying or curing process, making it possible to remove the primer process. As a result, it has been possible to achieve a light interception function with color variations. Figure 12 shows the content of the paint. To provide an example of the interception function, Fig. 13 shows light transmittance when the 1 base is made of a neutral color.

5.2. Results of Verification of Weather Durability

The paint content designed in this research was subjected to an outdoor exposure test, and no peeling of the coating was observed (Fig. 14).

Clear	30 μm	Appearance, Weather durability
2Base	12 μm	Coloring
1Base	25 μm	Light interception, Chip resistance
E-coat	20 μm	Corrosion control
Steel		

Fig. 12 Standard layer structure of 3C2B paint system of Honda

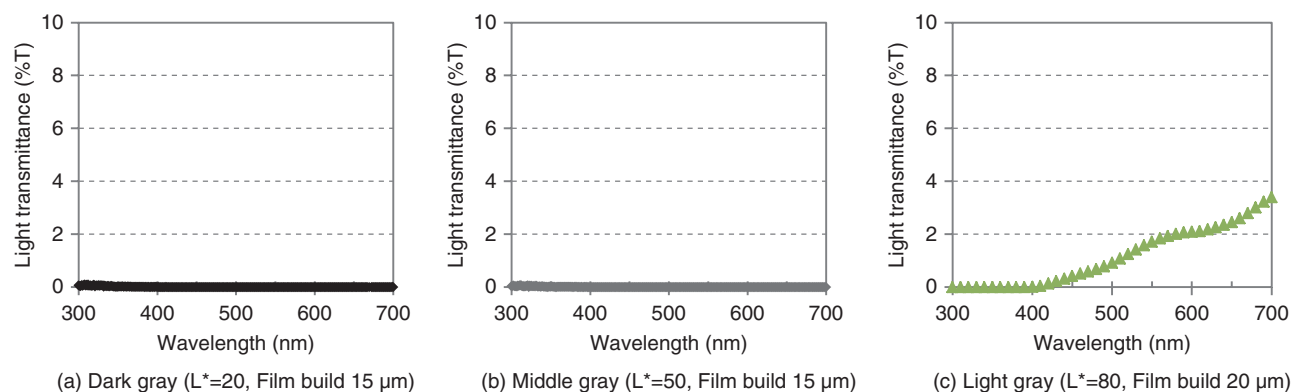


Fig. 13 Light transmittance of 1BC

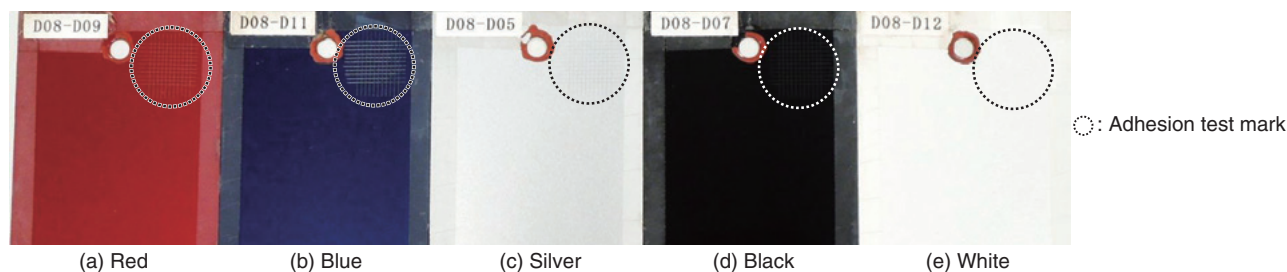


Fig. 14 Result of exposure test

6. Conclusion

The photo-degradation behavior of an E-coat was analyzed and the countermeasure was determined. The results are as follows.

- (1) A decline in the film strength of the E-coat was observed as a result of irradiated wavelength of 450 nm and below.
- (2) Cleavage of the bonds in the bisphenol binder of the E-coat was observed as a result of irradiated wavelength of 550 nm and below.

Based on these results, a layer able to stably intercept light of wavelengths of below 550 nm (1 base) has been applied before the color-developing layer (2 base), making application possible without processes such as drying, reconciling the removal of the primer process with color variations. This has reduced both the length of the paint process and CO₂ emissions against the conventional paint process.

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